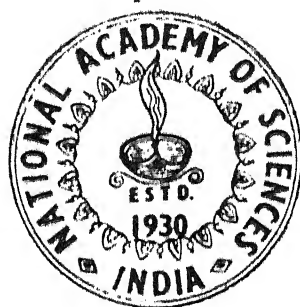


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PART I



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PART I

TYPES OF SECONDARY ALKALINIZATION OF SOILS IN THE IRRIGATED ZONES OF THE REGION OF THE GREAT HUNGARIAN PLAIN BEYOND RIVER TISZA

By

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ABSTRACT

1. The area of irrigated territories increased in Hungary to a great extent in the recent years. For the time being, 70—75 per cent of the irrigated areas are located in the region beyond river Tisza. The majority of the irrigated soils in this region belong to meadow type soils. When drainage is not carried out with a satisfactory care or irrigation is not adequately applied, soil waters of alkaline nature may rise and the possibility of a secondary alkalization must be considered.

Investigations were undertaken in different parts of the region beyond river Tisza with a view to study the effect of irrigation on the conditions of alkalization of the soils of meadow type in this region.

In the course of our investigations, three distinct forms of secondary alkalization were classified :

- (a) Accumulation of neutral alkali salts in the topsoil layers, i.e. a secondary salinization of soil.
- (b) Accumulation of neutral salts of alkali and alkali earth metals in the deeper horizons of the soil.
- (c) Increase of the content of exchangeable sodium ions of the soil, i.e. a secondary solonization (alkalinization).

2. The three types of secondary alkalization observed not only differ in the conditions of their formation but require also various methods for proper reclamation.

In regions where neutral salts of alkali and alkali earth metals accumulate in deeper soil horizons, it is satisfactory to prevent further accumulation of salts and the appearance of a secondary salinization by a careful drainage, adequate agrotechnique and proper crop rotation.

On reclaiming secondarily solonized soils, it is necessary to lower the level of soil water, together with the simultaneous application of chemical reclaiming agents. In the case of soils subjected to secondary salinization, favourable effects can be expected by lowering the level of soil water, removing soluble salts and simultaneous application of adequate chemical reclaiming agents.

The area of the irrigated zones in Hungary increased in recent years to an appreciable extent. Recent hydrotechnical instalments secured the minimum requirements of technical equipment necessary for the irrigation of an area of about 300000 cadastral "hold" (1 cadastral "hold" being equal to 0.57 ha), whilst the actual area irrigated amounted in 1957 to 220000 cadastral "hold". About 70-75% of these irrigated zones are located in the region of the Great Plain beyond river Tisza.

The majority of the soils actually irrigated or planned to be irrigated belong to meadow type soils: being meadow soils, solonetz meadow soils and meadow solonetz. In the formation of all these soil types, water conditions of the Great Plain plays a considerable role. The high level of the water table appreciably affects the formation of the soil characteristics for the time being as well. The effect of water conditions and of soil waters of high salt content of the Great Plain on the meadow alkali soils of this region in the past and in the present is equally of particular importance.

The interaction of water and formation of alkali soils has already been discussed by a number of foreign authors, as Kovda¹⁸, Gedroiz¹¹, Glinka¹² and Kelley¹⁷ as well as Hungarian authors, as Muraközy²¹, Sigmond^{26,28}, Treitz^{36,37}, Mados^{19,20}, Scherf²⁴, Endrédy¹⁰, Arany^{31,5} and Szabolcs^{30,32}, who examined the problem of formation of alkali soils from diverse points of view and often evaluated the results obtained from different aspects. In general, however, all the mentioned authors consider alkali soils as being formed under the effect of particular conditions of water and salt movement.

Thus, Gedroiz¹¹ attributes the formation of certain types of alkali soils to the accumulation and subsequent elution in an alkaline medium of soluble salts. Of the Hungarian authors, Sigmond^{24,28} and of the Soviet authors, Kovda¹⁸ are of a similar opinion. Glinka¹², in turn, explains the formation of alkali soils of the solonetz type by the alternation of the rise of the level of alkaline soil waters and of the elution of soluble salts from upwards, i.e., by the alternate direction of the movement of dilute salt solutions in the soil profile.

The study of alkali soils is discussed in the Hungarian literature of soil science to an appreciable extent, the earliest investigations being made almost a century ago. The classical authors of Hungarian soil science, as József Szabó²⁹, Muraközy²¹, Treitz^{36,37} and Sigmond^{26,27,28} devoted the major portion of their scientific activity to the elucidation of the conditions of formation and of the properties of Hungarian alkali soils. The investigations of these research workers, together with the later work of Mados²⁰, Scherf²⁴ and Endrédy¹⁰ proved that the properties and the direction of development of these alkali soils can decisively be influenced by the control of their water and salt movement. Two fundamental methods are known for the control of the water economics of soils: drainage and irrigation.

The extensive flood control and drainage work carried out in Hungary in the second half of the last century altered appreciably the hydrological conditions of the drained regions²². Besides, by drainage, also the soil conditions, particularly the properties and regional occurrence of alkali soils were markedly affected. Obviously, the process of formation of alkali soils started much prior to drainage. However, the present form of Hungarian alkali soils was fashioned after, and under the effect of the alteration of the hydrological conditions of the Great Plain.

Irrigation represents another factor of extreme importance from the aspect of the water and salt metabolism of soils. In Hungary attempts were made at the time of starting the irrigation, to combine irrigation and its harvest increasing

action with the reclamation of alkali soils and to include irrigation in the system of this reclamation plan. The reclaiming action of irrigation on alkali soils has already been pointed out by Sigmund²⁵ and Gyárfás^{13,14}, whilst later Herke^{15,16} and Prettenhoffer²³ attained appreciable harvest responses in certain types of alkali soils, by combining chemical methods of soil reclamation and irrigation.

However, irrigation and particularly, irrigation in an improper way, often have detrimental effects. A number of foreign and Hungarian instances indicate the formation of smaller or larger areas of alkali soil, due to irrigation effects. Under certain conditions, soluble salts may migrate into the top layers of the soil profile, and may accumulate there. This type of formation of alkali soils, provoked by irrigation and characterized by the presence of salt accumulation, is denominated by Kovda¹⁸ as secondary salinization of soils. A similar process of the accumulation of salts due to irrigation is also mentioned by Kellpy¹⁷. In order to prevent this effect, both authors are of the opinion that, in addition to securing adequate drainage conditions, the control of the salt content of irrigation water is necessary or, in other words, that water is suitable for irrigation up to certain salt content only. Under conditions prevailing in Hungary, irrigation waters should not contain more than 500 mg salt per litre. Kelley¹⁷ and Thorne and Peterson³⁵ consider, besides the total salt content and the electric conductance value of irrigation waters, the relative quantity of sodium ions, expressed as a percentage of the quantity of total cations for the evaluation of irrigation waters. Mados¹⁹ and Arnay⁴ are of the same opinion. The content of sodium ions expressed as the percentage of total cations is denoted by Arnay as quotient of alkalization, which is considered to be one of the most important parameters of irrigation waters. According to these authors, the knowledge of the quotient of alkalization is necessary as the cations of irrigation waters are presumed to enter an interaction with the exchangeable bases of soils. In the case of irrigation waters containing relatively greater amounts of sodium ions, the content of exchangeable sodium ions of the soils may increase under the effect of irrigation. Accordingly, in their opinion, a natural water is only suitable for irrigation when its interaction with the soil does not lead to an increase in the content of exchangeable sodium ions in the soil, i.e., when no process of alkalization starts in the soil in contact with irrigation water. Thus, it is clear that, according to these authors, in addition to salt accumulation, another form of secondary alkalization, namely, the saturation of the colloidal complex of the soil by sodium ions is considered a practical possibility.

Our investigations carried out in recent years in the irrigation areas and in their vicinity^{6,7,30,31} pointed to the oft occurrence of the accumulation of soluble salts to a smaller or greater extent in these areas. In our opinion, the accumulation of soluble salts in the examined territories was not mainly caused by the high salt content of irrigation water but rather by the deteriorating effect exerted by poor conditions of drainage, high rates of irrigation, excess flooding, leakage of channels, etc. leading to fluctuations in the level of soil water. Our investigations proved^{8,9,32,34} that the level of soil water, and the chemical composition of soil water, together with the quantity and qualitative composition of soluble salts in the soil and their distribution in the soil profile disclose definite periodicity. It was even found that soluble salts accumulated in one season and eluted in another. The seasonal alternation of these processes can also be observed in non-irrigated meadow soils. However, in irrigated areas and in their vicinity, the movement of the soluble salts of soils attains a rather greater extent, and a secondary alkalization of soils often occurs, provoked either by the accumulation of soluble salts or by the interaction of the liquid and solid phases of the soil.

In the course of our observations, three distinct forms of secondary salinization were discernible in the territories examined.

1. **Accumulation of Neutral sodium salts in soil surface**—This means that, in certain cases, the accumulated soluble salts may reach the surface soils and may attain a level detrimental to plant growth. It was observed in a rice plot of the State Farm Hortobágy that this form of secondary salinization under the effect of irrigation accumulated a great amount of soluble salts in soil surface, provoking a secondary salinization of soil. In the examined plot rice was grown also in previous years. As the plot was not ploughed in May, the efflorescence of soluble salts was clearly observable. The soil belonged to the type of meadow solonetz with a rather thin 5–10 cm horizon "A" below which followed a compact accumulation horizon of about 50 cm thickness. The level of soil water was near the surface (100–150 cm.)

TABLE 1
Data of the analysis of the aqueous extract of soil profile Hortobágy 1003

		Alkalinity									
Date of sampling	Depth of horizen (cm)	Dry matter (%)	Nor- mal CO ₃	Alkali		Total HCO ₃	Cl ⁻	SO ₄ ⁼⁼	Ca ⁺⁺	Mg ⁺⁺	Na ⁺
				metal Na HCO ₃	earth metal Ca(H CO ₃) ₂						
mg equiv./100 g of soil											
May 8, 1956.	0- 20	0.57	..	2.23	0.35	2.58	0.78	6.41	0.47	0.07	6.62
	20- 40	1.58	..	0.56	0.29	0.86	1.24	31.75	2.84	1.38	19.76
	40- 60	0.43	0.19	1.15	0.03	1.19	1.55	11.77	0.34	0.15	10.18
	60- 80	0.59	0.23	1.45	0.04	1.49	1.72	7.85	0.28	0.05	9.25
	80-100	0.50	0.23	1.05	0.02	2.07	1.64	4.83	0.19	0.06	7.28
	100-120	0.46	0.35	2.45	0.21	2.66	1.50	4.15	0.19	0.07	6.22
	120-140	0.33	0.35	2.43	..	2.43	0.96	3.19	0.14	0.13	4.81
June 20, 1956.	0- 20	0.53	..	1.66	0.58	2.25	0.30	4.55	0.65	0.09	5.74
	20- 40	0.67	0.12	2.54	0.02	2.56	0.24	7.00	0.31	0.09	7.46
	40- 60	0.51	0.16	1.72	0.09	1.82	0.26	7.82	0.22	0.18	9.25
	60- 80	0.28	0.19	2.47	0.07	2.54	0.26	3.90	0.18	0.09	3.50
	80-100	0.38	0.00	1.14	0.19	2.03	0.24	4.24	0.34	0.07	5.25
	100-120	0.38	0.23	2.52	0.05	2.58	0.26	2.02	0.31	0.03	5.52
	120-140	0.34	0.27	2.82	..	2.88	0.36	1.43	0.17	0.07	5.41
July 30, 1956.	0- 20	0.63	..	1.19	0.23	1.43	0.52	12.66	0.71	0.36	8.62
	20- 40	1.12	..	0.47	0.44	0.92	0.66	28.51	2.31	0.40	14.03
	40- 60	0.92	..	0.64	0.21	1.86	1.04	15.60	0.47	0.45	13.98
	60- 80	0.66	..	1.70	0.05	1.76	1.10	14.54	0.33	0.21	10.05
	80-100	0.88	0.10	2.23	0.15	2.39	1.14	0.99	0.28	0.24	9.27
	100-120	0.39	0.16	2.48	0.17	2.66	0.94	0.46	0.20	0.22	6.55
	120-140	0.39	0.19	2.82	0.29	3.11	0.88	0.77	0.20	0.12	6.00

The plot was ploughed in the second half of May, when rice was sown and the plot was immediately flooded. Rice germinated very poorly in the whole plot, large spots remained quite empty. Therefore, flood water was removed in July. When the soil became dry, the salt efflorescence reappeared. On the basis of observations on the spot it was quite clear that the germination and growth, respectively, of rice was impeded by the high content of soluble salts in the top horizon of soil. This was supported by the data of the chemical analysis of the aqueous extract of soil.

The first sampling was carried out on May 8, prior to ploughing the rice plot. The quantity of soluble salts of the soil was considerable, exceeding 0.5% in the 20 cm. topsoil layer, whilst in the next layer (20—40 cm. depth), the content of soluble soils ranged over 1.5%. The soluble salts mainly consisted of sodium sulphate with a little sodium chloride and sodium bicarbonate. The fact that the majority of sodium salts are neutral is of great importance from two points of view :

- (a) Owing to their fair solubility, sodium salts are extremely mobile. Thus, they are easily lifted to the topsoil layers by the rise of the level of soil water. When the level of soil water is near, they can only temporarily be eluted, to a limited extent.

According to the data of Table 1, samples taken at the next date, June 20, i.e. three weeks after flooding the rice plant, disclose smaller amounts of soluble salts in the soil profile, obviously under the effect of flood water. When, however, flood water was let off, the content of soluble soils recovered its former high level in the soils. As proved by the data of the chemical analysis of the aqueous extracts of samples taken on July 30, it nearly attained the level observed prior to flooding. Simultaneously with the rise of the soluble salts, the salt efflorescence in the surface of soil reappeared.

TABLE 2

Chemical composition of the Hortobagy salt efflorescence

Carbonate	..	Nil	
Bicarbonate	..	0.81	mg. c./litre
Chloride	..	3.10	"
Sulphate	..	112.39	"
Calcium	..	1.53	"
Magnesium	..	14.23	"
Sodium	..	111.82	"

According to the data of chemical analysis (Table 2) the chemical composition of salt efflorescence is identical to that of the soluble salts of soil, mainly consisting of sodium sulphate.

- (b) It indicates that the concentration of salts in the soil solution is already high at a relatively low content of moisture.

It follows from the recalculation of the data of Table 3, that at a moisture content of 19.4%, about 50% of the soluble salts is contained by the soil solution in the 20 cm. thick topsoil layer. These data prove that the accumulation of soluble salts takes place in the soil under the effect of the adjacent soil water. Accordingly, an efficient and durable soil reclamation is only possible when the level of soil water is lowered. This first step must be followed, as the salt accumulation took place in a solonetz soil,* by the removal of soluble salts and by a chemical soil reclamation.

TABLE 3

Chemical composition of the soil solution of soil profile Hortobagy 1003

Date of sampling	Depth of horizon, (cm)	Moisture (%)	CO ₃ ⁻⁻	HCO ₃ ⁻⁻	Cl ⁻	SO ₄ ⁻⁻	Ca ⁺⁺	Mg ⁺⁺	Na ⁺
			mg equiv./l						
May, 8, 1956	0-20	19.4	..	7.99	44.4	194.93	10.77	10.50	168.41
	20-40	15.4	..	3.75	81.4	182.04	12.19	10.14	180.88
	40-60	16.9	..	4.64	99.1	114.03	11.30	16.77	181.91
	60-80	15.1	..	3.98	124.2	109.34	10.70	3.03	178.89
	80-100	17.2	..	4.62	100.8	140.03	3.99	3.37	174.89
	100-120	21.8	0.75	8.20	22.2	56.85	1.60	1.77	141.96
	120-140	19.4	0.22	7.91	60.8	38.65	0.99	0.82	96.08

2. Accumulation of salts of alkali and alkali earth metals in the deeper horizons of the soil.—A case of this type occurred in plot II/1 of the Experimental Farm at Szarvas where soil investigations were carried out by us under clover as dominant plant, after several years of rice production.

TABLE 4

Chemical composition of the aqueous extract and of the soil solution of soil profile Szarvas 14

Depth of horizon (cm)	Dry matter (%)	HCO ₃ ⁻⁻	CO ₃ ⁻⁻	Cl ⁻	SO ₄ ⁻⁻	Ca ⁺⁺	Mg ⁺⁺	Na ⁺
		mg equiv./100 g of soil						
0-20	0.26	0.43	..	0.11	4.49	0.67	0.96	3.39
20-40	1.63	0.25	..	0.09	22.79	9.21	4.43	9.50
40-60	0.75	0.44	..	0.09	11.49	1.10	1.17	9.75
60-80	0.46	0.82	..	0.09	6.99	0.17	0.34	7.39
80-100	0.46	0.84	..	0.09	6.62	0.17	0.31	7.07
100-120	0.42	0.98	0.11	0.14	10.47	0.17	0.44	10.98
120-140	0.41	0.88	..	0.09	5.08	0.14	0.19	5.73

	Moisture (%)	Analysis of soil solution, mg equiv./l						
		CO ₃ ⁻⁻	HCO ₃ ⁻⁻	Cl ⁻	SO ₄ ⁻⁻	Ca ⁺⁺	Mg ⁺⁺	Na ⁺
0-20	18.2	2.15	..	15.40	17.43	7.52	2.78	16.18
20-40	21.4	2.93	..	11.36	54.24	16.80	5.76	41.02
40-60	23.1	4.77	..	13.80	44.39	3.42	3.08	58.30
60-80	24.6	5.78	..	12.80	60.35	2.24	2.74	17.79
80-100	25.2	7.46	..	4.60	69.72	2.06	2.62	83.67
100-120	25.7	5.42	..	3.50	91.78	2.28	3.33	82.67
120-140	27.9	3.91	..	3.14	81.21	2.71	3.77	82.58

The data of the chemical analysis of the aqueous soil extract (Table 4) show that the 20 cm thick topsoil layer contains only 0.2% of soluble salts. The maximum of salt accumulation appears in the depth 20-40 cm. where the content of soluble salts is rather high. However, it is of interest to study the chemical composition of these salts in detail. In contrast to the Hortobágy soil profile, where 95-96% of soluble salts consisted of sodium salts, the supply of soluble salts includes in the present case, particularly in the accumulation horizon, relatively much calcium and magnesium salt. The fact that the major portion of the supply of soluble salts in the soil consists of poorly soluble salts of alkali earth metals, refers to the phenomenon that, at the same content of moisture, only a lower percentage of soluble salts is actually present in the solution than in the case of soils where sodium salts predominate. The data of the chemical analysis of the soil solution of the Szarvas soil profile clearly show that it possesses a markedly lower concentration than that of the Hortobágy soil profile. On recalculating the analytical data we find that, at a nearly identical content of moisture, a markedly lower percentage of soluble salts is actually present in the solution than in the case of the profile where sodium salts are predominant.

TABLE 5

Changes in the content of total gypsum and CaCO_3 of the soil profiles examined

Location and file number of profile	Depth of horizon (cm)	Total CaSO_4 (%)			Total CaCO_3 (%)		
		May 8	June 20	July 30	May 8	June 20	July 30
Hortobágy 1003	0-20	0.53	0.20	0.14	1.11	1.25	0.95
	20-40	0.24	0.28	0.13	11.68	11.59	13.01
	40-60	0.63	0.33	0.35	27.55	30.41	18.18
	60-80	0.58	0.16	0.30	23.34	23.35	15.88
Szarvas 14		July 15	Aug. 23	Oct. 9	July 15	Aug. 23	Oct. 9
	0-20	0.062	0.054	0.093	4.77	5.32	5.31
	20-40	0.126	0.349	0.095	4.05	7.18	5.23
	40-60	0.063	0.090	0.185	4.82	10.82	12.97
	60-80	0.057	0.093	0.225	5.49	19.28	18.75
Kopáncs 301		May 19	July 13	Aug. 31	May 19	July 13	Aug. 31
	0-20	..	0.074	0.025	..	4.80	4.60
	20-40	0.069	0.058	0.028	4.04	7.40	4.20
	40-60	0.119	0.219	0.069	4.42	12.03	6.63
	60-80	0.368	0.158	0.168	11.29	19.20	15.90

This partially means as well that, when a portion of soluble salts consists of poorly soluble salts of alkali earth metals, the supply of soluble salts in the soil is appreciably less mobile. This is one of the causes why the accumula-

tion of soluble salts during irrigation did not reach the surface of soil. Another cause is that relatively favourable drainage conditions existed in the Experimental Farm at Szarvas. As a result of these, the level of soil water, which rose during the irrigation season, re-occupied nearly the original low level after the end of irrigation. It must be noted that the conditions of salinization of the soil and the mobility of calcium compounds are markedly affected by the presence of sodium carbonate and by the quantity of sodium bicarbonate even in the case when their amounts are small in absolute value. This can well be seen from Table 5.

The data of Table 5 show that the total quantity of gypsum in the Hortobágy profile exceeds that of the Szarvas profile. However, the effect of gypsum is markedly stronger in this latter case, which may be ascribed to the lack of sodium carbonate and to the smaller quantity of sodium bicarbonate present. To prove this, the solubility of gypsum was measured in dilute solutions of sodium bicarbonate of various concentration. The obtained values are presented in Fig. 1.

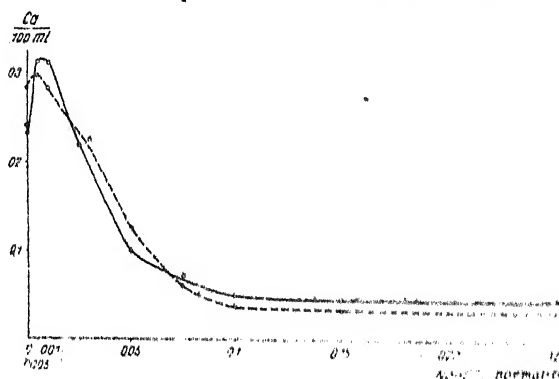


Fig. 1

Changes in the solubility values of gypsum plotted against changes in the concentration of a solution of NaHCO_3

As can be seen in Fig. 1, the solubility of gypsum appreciably decreases with the rise of the concentration of sodium bicarbonate. The reduction of the solubility values of gypsum with the rise of the concentration of sodium bicarbonate explains why calcium sulphate plays a more important role in the Szarvas soil profile where the amount of gypsum is smaller but the content of bicarbonate lower, in contrast to the Hortobágy profile where, whilst the content of gypsum is higher, the quantity of sodium bicarbonate is at the same time greater and sodium carbonate appears as well.

These observations also point to the fact that the changes in the quantity of calcium sulphate in the aqueous extract of the soil during irrigation may be attributed to two factors :

- (a) Movement of gypsum in the soil profile, depending on the water movement in the soil.
- (b) Changes in the solubility of gypsum, depending on the quantities of sodium carbonate and sodium bicarbonate present. The changes in the content of gypsum in the aqueous extract of soil profile Hortobágy 1003 (Table 1) represent a characteristic example of this case.

As the data of Table 1 show, the accumulation horizon (20–10cm) contained, prior to flooding the plot, relatively much calcium sulphate. On flooding, this quantity decreased, together with the rise of the amount of bicarbonate and the appearance of sodium carbonate whilst the total quantity of gypsum in the soil profile did not markedly change at the same time. After removing irrigation water, alkalinity due to sodium carbonate disappeared, the concentration of sodium bicarbonate diminished. In this way, the solubility of gypsum once more rose, and its quantity in the aqueous soil extract nearly regained the initial level.

All the mentioned data disclose that the solubilities of the components of the supply of soluble salts in soils are affected by each other. Further, as will be seen later on, there exists an interaction with the solid phase of soils and, through this action, also with their effect on the conditions of alkalinization.

3. Secondary solonization (alkalinization) of irrigated soils.—In this case, the quantity of exchangeable sodium ions of soils increases under the effect of irrigation whilst only a rise of small extent takes place in the amount of soluble salts although the level of soil water is near. Soil profile Kopáncs 301, taken in a rice plant several years old, belongs to this type.

TABLE 6

Chemical composition of the aqueous extract of soil profile Kopáncs 301

Date of sampling	Depth of horizon (cm)	Dry matter (%)	Alkalinity			Cl ⁻	SO ₄ ²⁻	Ca ⁺⁺	Mg ⁺⁺	Na ⁺
			Alkali metal Na HCO ₃	Alkali earth metal Ca- (HCO ₃) ₂	Total HCO ₃					
mg equiv. %										
May 19, 1956.	0- 10	0.15	0.56	0.21	0.77	0.30	1.86	0.40	0.28	1.51
	10- 20	0.27	0.61	0.35	0.97	0.38	1.37	0.48	0.26	1.40
	20- 40	0.19	0.77	0.25	1.03	0.38	1.47	0.27	0.24	2.00
	40- 60	0.24	0.89	0.37	1.27	0.58	1.66	0.44	0.14	2.05
	60- 80	0.34	0.90	0.27	1.18	0.66	1.96	0.39	0.14	2.43
	80-100	0.34	1.33	0.25	1.59	0.98	3.85	0.44	0.24	4.79
	100-120	0.40	1.43	0.42	1.85	0.20	3.00	0.42	0.07	4.16
	120-140	0.39	1.45	0.36	1.81	1.74	3.64	0.30	0.16	5.63
	0- 10	0.30	1.07	0.88	1.90	0.60	0.92	0.48	0.14	2.72
	10- 20	0.30	1.05	0.72	1.76	0.58	0.77	0.33	0.12	2.40
	20- 40	0.25	1.11	0.76	1.88	0.74	1.25	0.41	0.14	2.67
	40- 60	0.31	1.31	0.82	2.13	0.88	1.14	0.42	0.08	3.54
	60- 80	0.55	1.68	0.33	2.01	2.04	4.12	0.32	0.14	8.78
	80-100	0.50	1.31	0.47	1.78	2.86	5.30	0.25	0.28	8.46

According to the data of the analysis of the aqueous extract (Table 6), the content of soluble salts ranges 0.2% in the upper and 0.4% in the deeper horizons of the soil. An appreciable portion of the soluble salts consists of bicarbonate, mainly of sodium whereas the amount of chlorides and sulphates raises only in horizons below 80 cm.

The quantity of soluble salts does not markedly change in the soil under the effect of irrigation although the level of soil water is not far. On comparing the chemical composition of the aqueous extracts of samples taken in May, prior to flooding, and of those taken at the end of August, after flooding for three months, almost no changes in the amount of soluble salts may be observed. In deeper soil horizons (below 60-80 cm), the quantity of sodium sulphate and sodium chloride slightly increased whilst that of sodium bicarbonate somewhat increased in the whole profile, and the bicarbonate character of the soil became more prominent. This character manifests itself in the chemical composition of the soil solution as well.

TABLE 7

Chemical composition of the soil solution profile Kopancs 301

Date of sampling	Depth of horizon (cm)	Moisture (%)	CO ₃ ²⁻	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	Ca ⁺⁺	Mg ⁺⁺	Na ⁺
mg equiv./l									
April, 1956.	0- 10	23.3	0.29	3.45	10.32	6.74	5.77	1.93	19.61
	10- 20	22.4	..	2.27	6.12	0.53	1.85	0.58	14.31
	20- 40	24.9	0.26	3.75	27.38	0.39	1.17	0.62	46.45
	40- 60	24.4	1.64	6.50	15.40	0.79	1.21	0.57	33.14
	60- 80	21.5	..	2.26	48.80	9.39	1.56	1.13	75.65
	80-100	20.6	..	1.86	68.74	70.22	4.35	2.67	136.86
August, 1956.	0- 10	41.0	..	10.78	12.00	7.39	3.20	1.18	30.99
	10- 20	40.2	..	5.52	15.80	14.78	1.56	0.64	35.22
	20- 40	34.7	..	7.32	27.80	23.35	1.78	1.21	57.96
	40- 60	26.4	..	4.72	80.46	6.77	4.06	1.66	83.04
	60- 80	21.3	..	2.92	88.50	92.76	8.37	7.28	167.21
	80-100	20.9	..	2.42	94.20	95.73	9.65	11.63	180.58
	100-120	27.2	..	2.92	136.00	90.57	11.60	4.72	194.18
	120-140	29.2	..	2.62	198.60	45.26	16.16	16.47	200.43

As is evident from Table 7, the quantity of easily soluble sodium chloride is predominant. However, in comparison to the data of the former described soil horizons, the relative quantities of hydrogen carbonates are appreciably greater. Sodium bicarbonate grows in importance, as proved by Figures 2, 3, 4, which give the chemical composition of aqueous extracts prepared from a Hortobágy, a Szarvas and a Kopancs soil at various soil : water ratios. It is clear that the Szarvas soil sample contained a maximum amount of calcium salts. However, with the rise

of the ratio water : soil, the quantity of calcium salts eluted from the soil proportionally increased.

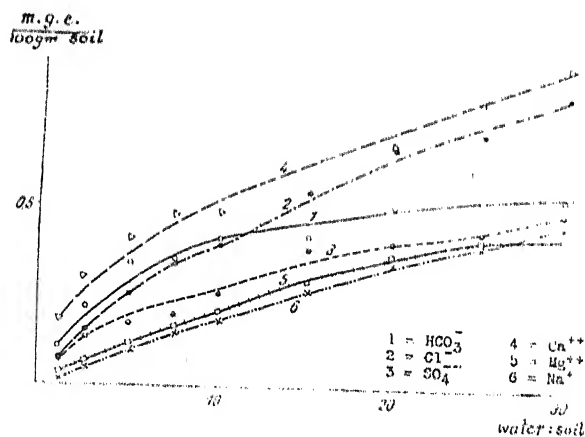


Fig. 2
Chemical composition of the aqueous extract at various ratios of soil : water (Szarvas)

In the Hortobágy sample, the quantity of calcium salts (which ranged much below that of sodium salts) eluted from the soil did not markedly rise over certain ratio of water : soil, whilst the rise of the quantity of sodium salts was found to be proportional to the increase of the ratios of water : soil. Here the sodium salts are mainly neutral ones, and the quantity of bicarbonate does not rise over certain ratios of soil : water. In the Kopáncs sample, the quantity of sodium salts shows a maximum. However, these salts mainly consist of bicarbonate, the reaction of which is known to be alkaline.

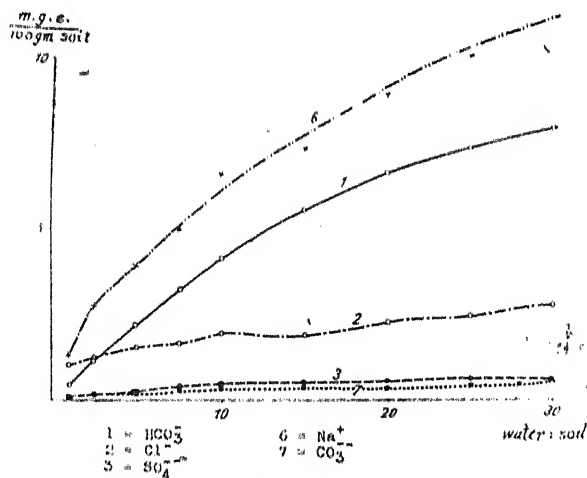


Fig. 3
Chemical composition of the aqueous extract at various ratios of soil : water (Hortobagy)

This relatively higher quantity of sodium bicarbonate refers to the possibility of the occurrence of the second form of alkalization, namely, to the secondary solonization of soils. This is supported by the markedly high relative content of exchangeable sodium ions in the Kopáncs soil profile.

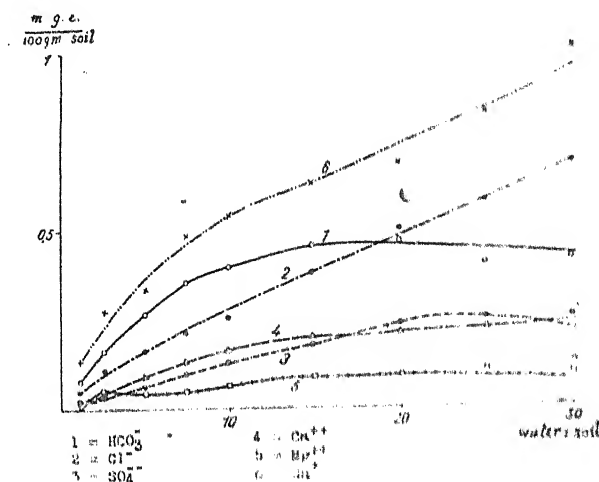


Fig. 4
Chemical composition of the aqueous extract at various ratios
of soil : water (Kopáncs)

TABLE 8
Content of exchangeable $\text{Na}^+ + \text{K}^+$ of soil profiles Szarvas 14 and Kopáncs 301

Date of sampling	File number of profile	Depth of horizon (cm)	Content of exchangeable $\text{Na}^+ + \text{K}^+$			Absorp- tion power
			mg %	mg equiv. %	Total %	
	Szarvas 14	0-20	135.66	5.9	24.3	24.27
		20-40	64.33	2.8	13.0	21.46
		40-60	123.87	5.4	20.6	26.08
		60-80	133.03	5.8	26.5	21.86
May 19, 1956.	Kopáncs 301	0-10	143.29	6.23	28.9	21.49
		10-20	212.98	9.26	35.2	26.32
		20-40	246.10	10.70	39.1	27.36
		40-60	344.08	14.96	60.0	24.71
		60-80	295.09	12.83	58.1	22.06
August 31, 1956.	Kopáncs 301	0-10	219.19	9.53	44.4	21.49
		10-20	289.57	12.59	47.9	26.32
		20-40	376.74	16.38	60.0	27.36
		40-60	382.72	16.64	67.4	24.71
		60-80	358.80	15.60	70.7	22.06

As can be seen in the data of Table 8, the content of exchangeable sodium ranges very high in the profile Kopáncs 301, attaining e.g., in the horizon 40-60 cm,

60% of the absorption power of soil. The content of exchangeable sodium increases in the soil to August, parallel to the rise of the amount of sodium bicarbonate, *i.e.*, the solonetz character of the soil increases.

The presumption that the absorption of sodium ions on the surface of the colloidal complex of soils is promoted by the presence of bicarbonate ions and the alkalinity of the medium, respectively, is also corroborated by comparing the quantities of exchangeable sodium ions in the Szarvas and Kopáncs soil profiles. As can be seen in Table 8, the relative amount of exchangeable sodium ions ranges in the Szarvas profile much lower, particularly in the horizon 20—40 cm, where (as was already previously shown by the data of chemical analysis of the aqueous extracts) a great amount of alkali earth sulphates is present.

It is striking that although the soil profile Szarvas 14 contains a large quantity of soluble salts which exceeds that of the Kopáncs profile, the relative quantity of exchangeable sodium ranges in this latter case much lower. This can only be ascribed to differences in the nature of soluble salts. In the Szarvas soils of sulphate character, the exchange reaction between the sodium ions of the soil solution and the exchangeable bases of the soil complex attains an equilibrium state even at a relatively higher concentration of sodium ions much quicker than in the case of the Kopáncs profile of bicarbonate character. The effect of anions on the equilibrium of the exchange reaction has already been pointed out by Antipov-Karataev¹ who attributed this effect to the differences in the solubilities of the compounds (CaSO_4 and MgSO_4 on one hand, and CaCO_3 and MgCO_3 , on the other) formed in the exchange reactions. This high relative quantity of exchangeable sodium, of the profile Kopáncs 301, results in the deterioration of the physical properties, mainly of the permeability of the soil. This may be one of the causes why no salt accumulation to a marked extent appeared during irrigation although the level of soil water was near. However, on irrigation, the quantity of exchangeable sodium ions increased with the rise of the amount of sodium bicarbonate, *i.e.* a secondary solonization of the soil took place. The three forms of secondary alkalization not only differ from each other in the conditions of their formation and in their properties, but also require different methods of reclamation.

When the salt accumulation does not reach the surface of the soil, and the majority of soluble salts consist of neutral alkali earth salts, the careful drainage of the irrigated zones is satisfactory, together with the reduction of leakages of channels and with securing an adequate agrotechnique for plant production.

When, however, a secondary solonization occurs during irrigation, the level of soil water must be lowered and at the same time, chemical ways of soil reclamation should also be applied. Whilst in irrigated areas where secondary formation of solonchak soils salinization appears, a successful and durable reclamation is only possible by following the technique: first applying methods to lower the level of soil water, then removing soluble salts and carrying out at the same time a chemical soil reclamation.

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DEGRADATION OF IRRIGATED RICE SOILS IN HUNGARY

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ABSTRACT

1. On the irrigated areas of the Hungarian lowland degradation of soil is very wide-spread and it exerts influence in an unfavourable way on the fertility of the soil.

2. Both the data of the 5 per cent KOH extract of the soil and the examination of exchangeable bases give evidence of the particular degradation in connection with alkalization. $\text{SiO}_2 : \text{Al}_2\text{O}_3$ of the soils in question is very wide, the exchangeable complex shows definite signs of degradation (decreasing S, increasing T S).

3. In irrigated soils the surface layer always shows the process of degradation contrary to soils degraded under dry conditions in which case A_2 layer often shows this maximum.

4. In consequence of degradation the physical, chemical and biological characteristics of the soil deteriorate from the fertility point of view.

5. Organic fertilization and plantation of leguminous plants decrease degradation.

In the last decade the irrigated growing of rice has become very wide-spread in Hungary. Formerly this culture was grown here only on very small areas. Rice is grown on the lowland of the country steppes. In general fields receive 500 mm. rainfall as a yearly average, the yearly average temperature is about 10°C . Naturally under such circumstances the long-growing-period rice types do not grow ripe on the Hungarian lowland, only ones with a shorter growing period grows. Rice sowing is in general in April, harvesting is in September-October.

Rice is mostly grown on alluvial and meadow soils of Hungary where the conditions of flood irrigation are ensured by the nearby rivers or by the canal-systems, which cover the lowland. These canal-systems were made mostly to meet the demands of rice cultivation. Rice is grown on more than 80 per cent of all irrigated territories in Hungary.

Most of the soils used for rice cultivation is alkaline. Among the exchangeable bases sodium is present in a significant quantity in these soils but it is often only 5-10 per cent though it exceeds 20 per cent in certain cases. These soils are usually rich enough in soluble salts but they rarely reach the surface layers and hence do not exert direct physiological influence on the life of the plant.

The quantity of salt rarely reaches 0.2 per cent in the surface layer, which is below the level of salt tolerance of rice plants, which therefore suffers no damage. Therefore in these alkaline soils rice cultivation is wide-spread. Analysis of the water soluble salts of such soils is shown in Table 1.

TABLE 1
The Analysis of Soluble Salts

Number and place of profile	Depth of Horizon (cm)	pH (H ₂ O)	Total HCO ₃	Cl	SO ₄	Ca ⁺⁺	Na ⁺	K ⁺	
			(%)	(%)	(%)	(%)	(%)	(%)	
23 Szarvas	Ap	2-12	6.8	0.063	0.004	0.013	0.36	0.20	0.13
	A	15-30	6.9	0.082	0.007	0.027	0.33	0.23	0.08
	B ₁	40-60	7.7	0.125	0.015	0.060	0.10	0.70	0.07
	B ₂	70-95	8.1	0.156	0.016	0.137	0.29	1.56	0.07
	C	105-120	8.5	0.214	0.017	0.069	0.12	1.32	0.06
	C	110-130	8.0	0.180	0.024	0.069	0.15	1.15	0.05
	C	140-160	8.5	0.186	0.010	0.066	0.09	0.83	0.05
	C	170-190	8.3	0.193	..	0.066	0.12	0.90	0.06
30 Szarvas	Ap	0-10	6.9	0.089	0.008	0.047	1.04	1.18	0.13
	A	12-28	6.3	0.081	0.008	0.047	0.69	0.23	0.09
	B ₁	40-60	6.5	0.076	0.007	0.047	0.19	0.33	0.05
	B ₂	70-90	6.5	0.082	0.009	0.040	0.34	0.38	0.06
	C	110-130	6.6	0.075	0.010	0.055	0.45	0.50	0.06
	C	160-180	7.3	0.102	0.011	0.054	0.45	0.17	0.07

TABLE 2
Exchangeable cations

Number and place of profile	Depth of Horizon (cm)	pH (KCl)	Hydrolytic acidity	Exchangeable cations %				
				Ca	Mg	Na	K	
23 Szarvas	A	2-12	5.90	0.66	70.09	24.89	3.53	1.47
	A	15-20	5.94	0.53	63.63	24.93	10.33	1.08
	B ₁	40-60	6.72	..	47.02	21.26	30.99	0.71
	B ₂	70-85	5.97	..	38.12	24.66	36.26	0.93

Distribution of the exchangeable bases is shown in table 2, where the solonetz character is clearly observable. Alkali soils in the alluvial plains of Hungarian lowlands where rice is grown belong generally to solonetz type. The formation of solonetz sole which was brought about as a result of the formation of the alluvial B layer and the leaching of the A layer goes together with further degradation of the material of the soil in certain cases. In consequence of this degradation the organo-mineral compounds of the soil disintegrate. Organic matter soluble in water is leached away in the course of erosion processes. The sesquioxide compounds of the mineral part are washed out in finer distribution into the alluvial layer and in the upper level of the soil the so called compounds of the amorphous silicic acid increase. This process is called by Sigmond the degradation of alkali soils; Gedroiz calls it solodisation.

Table 3 shows the analysis of 5 per cent KOH extract of some Hungarian alkali solonetz soil-types of which the two of Hortobágy are strongly solodised, but the soil of Szarvas is not. As it is seen, the rate $\text{SiO}_2 : \text{Al}_2\text{O}_3$ points this out well, because in case of strong solodisation the relative number is much higher than 2. From the table it is seen that the pH is nearly equal both in water and KCl. Solodization of alkali soils of the Hungarian lowland occurs due to the conditions of the momentary excess wetness. At such a time, usually in the wet periods of Spring and Autumn, wetness and water soaking the soil and filling in smaller depressions on its surface layer, create favourable conditions for the degradation of its material. Water accumulating on the alkali soils in the Hungarian lowland penetrates with difficulty into the profiles of the soil, as these soils have a very bad permeability. Table 4 shows the mechanical analysis of such a soil. The water having dried up, the surface of the soil, especially in the depressions, is covered with white dust, which in this case is not soluble salt, but so called amorphous silicic acid. A superficial look betrays the characteristics of the degradation of soil.

TABLE 3
Data of pH and 5 per cent KOH Solution of Solonetz Soils on the Hungarian Lowland.

Number and place of profile	Depth of Horizon (cm)	Soluble in KOH		Ratio $\text{SiO}_2 : \text{Al}_2\text{O}_3$	pH	
		SiO_2 (%)	Al_2O_3 (%)		H_2O	KCl
Hortobágy 24	A 2-10	3.96	0.260	13.0	6.9	6.1
	B 16-24	2.40	0.272	7.2	8.0	7.1
Hortobágy 113	A 3-12	4.42	0.254	14.8	6.7	5.9
	B 25-34	3.16	0.342	9.1	7.4	6.6
Szarvas 23	A 2-12	1.38	0.550	2.1	6.7	5.9
	B 40-60	1.75	0.790	1.9	7.7	6.5

TABLE 4

Mechanical Analysis of Hungarian alkali soils

Number and place of profile	Depth (cm)	Diameter of Aggregate mm						Lost on treatment with HCl (%)
		1-0.25 (%)	0.25-0.05 (%)	0.05-0.01 (%)	0.01-0.005 (%)	0.005-0.001 (%)	0.001 (%)	
Szarvas 23	2-12	0.24	11.70	33.01	10.05	11.41	31.50	2.09
	15-30	0.25	12.11	28.34	7.51	14.26	27.53	10.00
	35-50	0.36	4.01	27.83	8.25	12.07	43.45	4.03
	40-60	0.09	1.70	25.18	9.73	12.87	45.15	5.38
	70-90	0.10	1.39	30.55	7.34	13.29	34.51	13.12
	105-120	0.09	..	27.70	14.26	13.98	27.26	17.30
	140-160	0.11	..	37.25	10.32	15.14	26.08	11.50
	170-190	0.12	..	56.23	5.65	10.96	16.97	10.70

TABLE 5

SiO₂ and Al₂O₃ soluble in 5 per cent KOH

Number and place of profile	Depth of Horizon (cm)	SiO ₂ (mg.cq.)	Al ₂ O ₃ (mg.cq.)	SiO ₂ Al ₂ O ₃
Hortobágy	4-15	19.4	0.8	24.78
No. 144	30-40	9.2	4.9	1.89
No. 145	3-8	27.2	1.8	14.95
	18-22	20.2	0.7	29.40
	40-40	10.3	2.9	3.54
	60-65	8.3	4.6	1.81
No. 156	4-20	29.1	0.7	29.10
	35-45	7.9	2.1	3.92
	60-70	5.6	2.6	2.16
No. 147	3-14	21.4	5.5	3.74
	23-33	25.0	1.4	17.75
	40-48	9.6	3.1	3.18
	58-68	8.2	3.1	2.66
No. 148	4-14	17.1	2.7	6.36
	22-33	12.2	7.2	1.71
	38-48	9.7	6.9	1.40
Pusztábanréve	0-20	13.1	3.9	3.31
No. 140	20-40	8.6	2.9	2.89
No. 142	3-13	12.5	0.55	22.70
	23-35	9.6	1.32	7.28

In course of irrigated farming in Hungary it is a frequent experience that in a few years the irrigated rice fields lose their fertility. Some times the cause of this loss of fertility is the overweeding of the ground, in other cases salt accumulation due to secondary alkalization is so great in the surface layers that it hinders further growth. This latter process is very frequent in the ricefields of Hungary as the soil-water containing salts are situated near the surface layer in the rice fields (often 1-2 m. from the surface layer). This water level is raised due to the inundation irrigation. The salts rise to the surface from the salty subsoil due to capillary action.

Solodisation is well characterised by the quantity of SiO_2 dissolving in 5 per cent KOH as well as the ratio of $\text{SiO}_2 : \text{Al}_2\text{O}_3$ expressed in equivalent, which is given in Table 5.

Profile No. 144 (Hortobágy) is from a field where rice was in monoculture for 4 years. In the area of profile No. 148 after 4 years of rice, grassy clover was grown for 2 years and then after organic fertilization maize was planted. The area of profile No. 146 on the other hand was under wheat for several years, after 1 year under rice. We find that the $\text{SiO}_2 : \text{Al}_2\text{O}_3$ ratio in field after monoculture of rice are very high (profile No. 144) but they are high even if wheat is sown after rice (profile No. 146.) Contrary to this in case of profile No. 148, the grassy clover as well as organic fertilization lowers the $\text{SiO}_2 : \text{Al}_2\text{O}_3$ ratio which shows a degradation to a smaller degree. In the above profiles it can be observed that the most degraded are the upper layers while going downwards in the profile the $\text{SiO}_2 : \text{Al}_2\text{O}_3$ ratio decreases which is a measure of degradation. On the other hand in case of profiles 145 and 147 see the maximum degradation is not in the highest, but in the next layer as indicated by the $\text{SiO}_2 : \text{Al}_2\text{O}_3$ ratio. Profiles No. 145 is an unbroken original lawn and No. 147 is from a maize field which has not been irrigated since its first breaking up.

The above conclusions are also supported by the data of Pusztabánréve, (Table 5). Here in profile No. 142, great degradation is shown in the surface layer as a result of rice monoculture for 5 years. On the other hand in the area of profile 140 after 4 years of rice monoculture there is irrigated red clover. The beneficial effect of the leguminous plant appears in the narrowing of $\text{SiO}_2 : \text{Al}_2\text{O}_3$ ratio which quite agrees with the observations at Hortobágy.

The process of degradation is shown not only by the analysis of 5 per cent KOH extract, but by the experiments on the adsorption complex of the soil. In such cases value S (total exchangeable bases) decreased in the degraded layer, on the other hand value (T-S) which is the quantity of the adsorbed H ions increase, where T is the base exchange capacity.

In the surface layer of profiles 144, 146 and 148 (Table 6) value S decreased a great deal compared to other layers. That shows degradation with which it is intimately associated. In case of these soils in consequence of irrigation the surface layer was the most degraded. Contrary to this in profiles 145 and 147 where there was no irrigation and the maximum degradation is to be found not in the highest, but in the layer under this in the so called A_2 layer, neither value S decreased, nor value T-S increased. That phenomenon is explained by the fact that the above mentioned areas of the profiles are quite near to the irrigated fields. In connection with these the effect of irrigation is manifest in the environment alkalisng characteristic of secondary alkalization.

TABLE 6

Exchangeable cations

Profile	Depth of Horizon (cm)	pH (KCl)	Ca	Exchangeable Mg mg eq.	K + Na	S	T	T-S
Hortobágy 144	4-15	5.5	18.0	6.4	3.5	27.9	31.8	3.8
	30-40	5.9	12.9	23.2	8.7	44.8	47.2	2.4
Hortobágy No. 145	3-8	5.9	6.4	37.8	7.6	51.8	58.1	6.3
	18-22	5.9	6.4	72.0	7.8	86.2	89.5	3.3
Hortobágy No. 146	4-20	5.9	3.9	4.5	2.1	10.5	12.4	1.9
	35-45	6.1	2.4	17.9	7.1	27.4	29.5	2.1
Hortobágy No. 147	3-14	4.9	9.4	7.6	7.7	24.7	33.0	8.3
	23-33	5.3	2.4	12.9	3.2	18.5	28.0	9.5
Hortobágy No. 148	4-14	6.4	11.9	6.4	2.2	20.5	22.0	1.5
	22-33	6.4	16.3	22.4	6.3	45.0	47.3	2.3

Secondary alkalization *i.e.* salt accumulation goes with the filling up of the adsorption complex with cations, so neither value S decreases, nor value T-S increases. In these cases together with the natural degradation, other process, a secondary alkalization is observable on the fields surrounding the irrigation areas. This is supported by Figure 1.

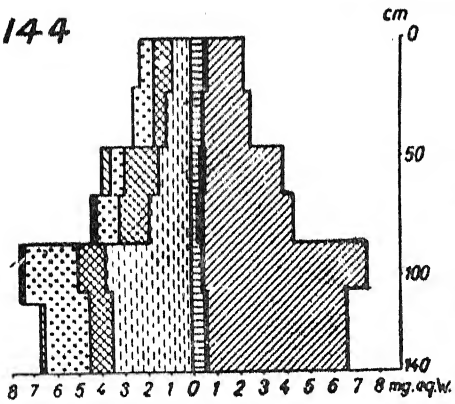
From the Figure 1 it can be seen that while in profiles 144, 146 and 148 soluble salt is less, although these were under irrigation, in profiles 145 and 147, which were near the irrigating system, soluble salts, especially the quantity of NaCl increases in a great deal in the surface layer.

From above detailed data it can be seen that this particular degradation of soil is a phenomenon due to the irrigation system in the Hungarian Lowland, which is considerably wide-spread and exert an unfavourable influence on the fertility of Hungarian irrigated fields. This process is unfavourable on the one hand because while making the organic matter soluble, a part of it disappears from the soil. Moreover, in consequence of degradation of colloid complex, not only the chemical and physical characteristics of the soil get worse but the structure-forming possibility and other physical characteristics too are adversely affected.

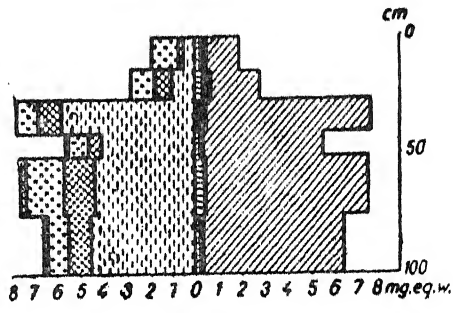
Excessive anaerobic conditions as well as the process of degradation influence in a detrimental way the microbiology of soil, a consequence of which in all probability appears in the mineralization and adaption of nutrition element, but in other process of the life of plants too. As our data prove, the organic fertilization and clover plantation have a good effect in compensating degradation to a certain extent.

SALT PROFILES

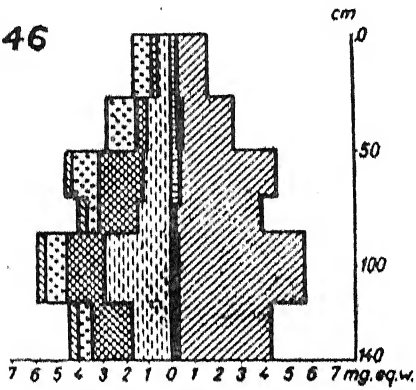
No. 144



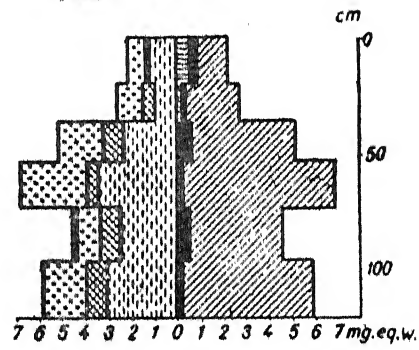
No. 145



No. 146



No. 147



No. 148

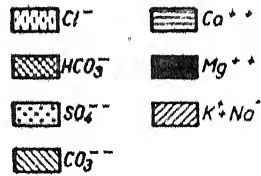
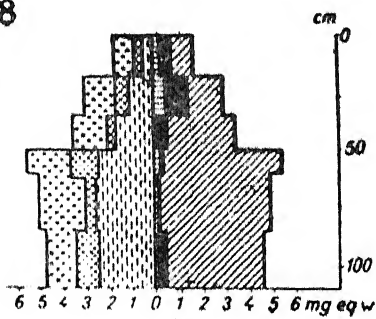


Figure 1

The soil improvement which has been on a large scale going on the Hungarian lowland for a long time compensates also for the process of degradation of soil. The improvement of Hungarian alkali soils of alluvial origin and acid surface soils takes places with materials containing lime, which makes the soil resistant against degradation. So numerous methods, for example the right plant rotation, fertilization and soil improvement offer to counter-balance this harmful process, perhaps it may be eliminated too.

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STUDIES ON THE UNSAPONIFIABLE MATTER OF THE SEEDS OF *CLITORIA TERNATEA* LINN. AND ISOLATION OF γ -SITOSTEROL

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[Received on January 25, 1960]

ABSTRACT

γ -sitosterol has been isolated from the seeds of *Clitoria ternatea* Linn. and has been characterised by the preparation of its acetate and benzoate derivatives and by comparing their percentage composition, m. p.'s and rotations with those for known sitosterols.

Clitoria ternatea Linn. commonly known as Aparajita belongs to *Papilionacea* sub-group of the *Leguminosae* family and is known for its medicinal properties^{1,2,3}. The seeds yield 18.78% of a fixed oil which contains 1.62% of an unsaponifiable matter. Although, investigations have been carried out on the leaves of this plant by Tewari and Gupta⁴, a survey of available literature reveals that no systematic chemical examination has been undertaken on the unsaponifiable matter of the seeds so far. The present communication is concerned with the studies on the unsaponifiable matter of the seeds of *Clitoria ternatea* Linn. and isolation of γ -sitosterol.

The sterol has been isolated by the usual procedure adopted for the purpose.^{5,6,7} The non-volatile, non-saponifiable fraction obtained by extraction of the liquor left after distillation with ether contained the sterol. From this fraction the pure sterol has been isolated by repeated crystallisation of the corresponding acetate and benzoate and by chromatography over Brockmann alumina column.

The sterol has been identified as γ -sitosterol by the preparation of acetate and benzoate derivatives and comparing their percentage compositions, m.p.'s and rotations with those for known sitosterols.

The sterol gave negative tests for N, P, S and halogen. It responded to Salkowski reaction and digitonin test and in the Liebermann Burchard reaction, the compound assumed a purple to blue and then green coloration. In the Steinkellner reaction, a purple coloration was observed which on exposure to light turned cobalt blue.

EXPERIMENTAL

Identification of sterol fraction

Powdered seeds (1 Kg.) of *Clitoria ternatea* Linn. were extracted with a large excess of petroleum ether (b.p. 40°—60°) in an all glass soxhlet for 36 hours. The oily product obtained after evaporation of the petroleum ether extract was treated with acetone and the residue was saponified with 4% alcoholic potassium hydroxide and the unsaponifiable matter exhaustively extracted with petroleum ether. The oily residue from the petroleum ether extract was hydrolysed by refluxing on a water

bath for 12 hours with a large excess of 20% alcoholic potassium hydroxide. After hydrolysis, the product was diluted with a little water and the alcohol was evaporated on a water bath with the addition of a corresponding amount of water from time to time. The alcohol-free alkaline solution was extracted several times with petroleum ether. The total ethereal extract after washing with water was distilled and the brown semi-solid residue was again refluxed with 20% alcoholic potassium hydroxide for 12 hours to hydrolyse any trace of unchanged fatty oil. The non-saponifiable portion after removal of alcohol was extracted with ether and the solvent distilled off when the crude sterol fraction was obtained.

The extract was refluxed with methyl alcohol for 6 hours and then kept at 0° for 20 hours when a white precipitate was obtained. The filtrate was concentrated and again kept at 0° for 30 hours when a second lot of the precipitate was obtained. The sterols thus obtained were combined and refluxed with methyl alcohol for 3 hours, the solution on being kept at 0° for 60 hours deposited shining plates in clusters. The product was collected, dissolved in petroleum ether (b.p. 40°-60°) and kept at 0° for 16 hours, when shining plates separated. These were washed with a little methyl alcohol and dried in vacuum. The sterol (1.35 g.), m.p. 138°-41° thus isolated was completely dried in a vacuum desiccator.

Purification of the sterol

The sterol fraction was purified by chromatography of the product over Brockmann alumina using petroleum ether (b.p. 40°-60°) and benzene and chloroform (3 : 2, v/v) successively as eluents. The benzene-chloroform fraction gave colourless shining plates of sterol. The product was crystallised several times from ether-alcohol mixture (1:1, v/v) and finally from methyl alcohol when colourless shining plates of γ -sitosterol, m.p., 145°, $[\alpha]_D^{18}$ -40°·0 (CHCl₃) were obtained. The petroleum ether fraction consisted of a waxy material melting indefinitely from 50°-60°. γ -sitosterol was freely soluble in benzene, chloroform, and petroleum ether; sparingly in cold methyl alcohol and ethyl alcohol. The sterol showed no alteration in specific rotation on crystallisation,⁸ yield 1.25 g. (0.125% on dry weight basis of seeds). Found: C, 83.98; H, 11.88%. Mol. Wt. (cryoscopic in benzene) 422. C₂₉H₅₀O requires C, 83.98; H, 12.15%. Mol. Wt. 414.

Preparation of sterol acetate

The sterol (0.5 g.) was heated under reflux with 1.5 c.c. of acetic anhydride and 1.5 c.c. glacial acetic acid at 140° for 3 hours in an oil bath. The reaction product was cooled and filtered from the separated plates which were dried over fused CaCl₂ in a vacuum desiccator. The solid acetate was washed with water and 20% alcohol. It was crystallised once from absolute alcohol, yield (80.5%) and finally fractionally recrystallised from methyl alcohol in colourless shining plates, m. p. 140°-41°, $[\alpha]_D^{18}$ -47°·0 (CHCl₃). Found: C, 81.00; H, 10.96%. C₃₁H₅₂O₂ requires C, 81.57; H, 11.47%.

Hydrolysis of sterol acetate

The sterol acetate (0.2 g.) was saponified with 10 c.c. of alcohol, 1.0g. potassium hydroxide and a few drops of water by heating on a water bath under reflux for 8 hours. After the hydrolysis, alcohol was removed, the residue diluted with water and was extracted with ether. On removal of ether, the sterol was

crystallised once from absolute alcohol and twice from alcohol-benzene mixture (1 : 1, v/v) in colourless shining plates, m. p. 145° , $[\alpha]_D^{18} -40^{\circ}0$ (CHCl_3). Found : C, 84.00; H, 11.88%. Mol. Wt. 418. $\text{C}_{29}\text{H}_{50}\text{O}$ requires C, 83.98; H, 12.15%. The regenerated sterol developed a purple to blue and then green colour with Liebermann Burchard reagent.

Preparation of sterol benzoate

The benzoyl derivative of the sterol was prepared by Callon's method⁸. Benzoyl chloride (0.25 c.c.) was added to an ice-cold solution of the sterol (0.1 g.) in dry pyridine (2.0 c.c.) and methyl alcohol (0.2 c.c.). The mixture was kept at 25° for 12 hours, decomposed by the addition of crushed ice, acidified with conc. HCl and extracted with ether. The ethereal extract was washed successively with dil. HCl, sodium carbonate solution, water and then dried over fused CaCl_2 . On removal of ether, the sterol benzoate was crystallised from a mixture of ethyl alcohol and ether (equal vols.) until no further alteration in specific rotation was noted. The sterol benzoate was obtained in colourless shining plates, m.p. 150° , $[\alpha]_D^{18} -14^{\circ}5$ (CHCl_3). Found : C, 83.27; H, 10.35%. $\text{C}_{38}\text{H}_{54}\text{O}_2$ requires C, 83.34; H, 10.49%.

Hydrolysis of sterol benzoate

The sterol benzoate (0.1 g.) was refluxed on a water bath with 5% alcoholic potassium hydroxide (50 c.c.) for an hour. The reaction mixture was cooled in ice-cold water and the separated sterol was washed with water. It was recrystallised from absolute alcohol and dried in vacuum. The recovered sterol had m. p. 145° , $[\alpha]_D^{18} -40^{\circ}0$ (CHCl_3). Found : C, 83.96; H, 11.85%. $\text{C}_{29}\text{H}_{50}\text{O}$ requires C, 83.98; H, 12.15%.

Preparation of sterol digitonide

The sterol digitonide was prepared by taking a saturated solution of the sterol (0.1 g.) in absolute alcohol at 56° and treating with an equal volume of digitonin solution in 90% ethyl alcohol. The product was refluxed on a water bath for an hour and then kept at 0° for 12 hours when the digitonide was obtained as a white powder. It was separated, washed with alcohol and dried, m. p. 220° (decomp.). Found : C, 61.80; H, 8.40%. $\text{C}_{29}\text{H}_{50}\text{O} \cdot \text{C}_{66}\text{H}_{90}\text{O}_{29}$ requires C, 61.91; H, 8.6%.

Hydrolysis of sterol digitonide

The sterol digitonide was dissolved in pyridine and digitonin precipitated with the addition of ether. The filtrate was extracted with dil. HCl to remove pyridine and then with water to remove HCl. The ether layer was separated and evaporated to dryness. The residue (regenerated sterol) was dissolved in methyl alcohol and crystallised when colourless shining plates, m. p. 144° , $[\alpha]_D^{18} -40^{\circ}0$ (CHCl_3) was obtained. The sterol showed no alteration in specific rotation on crystallisation by the technique of Anderson.⁹

ACKNOWLEDGMENT

The author is indebted to Dr. P. N. Wahi, M.D., M.R.C.P. (Lond.), F.N.I., and to Dr. N. K. Chowdhury, M.D., Ph.D. (Edin.), Professors of Pathology and Pharmacology respectively, Medical College, Agra for their constant encouragement.

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PHYSICO CHEMICAL STUDY OF COMPLEX FORMATION OF ZIRCONIUM WITH DICARBOXYLIC ACIDS

Part I : Complex Oxalates of Zirconium

By

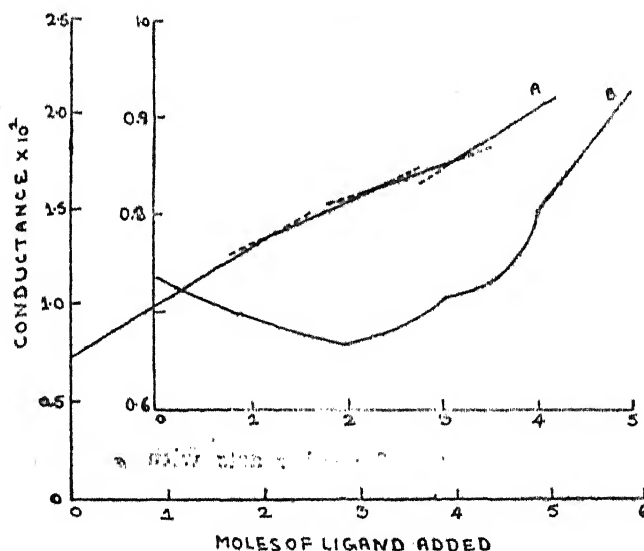
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[Received on January 27, 1960]

A great deal of work has been done on oxalates of zirconium. Howard S. Gable¹ analysed the white precipitate obtained by heating a mixture of zirconium chloride and oxalic acid solution in methyl alcohol and reported the composition of the white compound corresponded to be $Zr(OX)_2$. A. Rosenheim and P. Frank² prepared a series of complex 8- covalent oxalates of type $M_4Zr(OX)_4 \cdot xH_2O$ ($M=Na, K, NH_4$). In recent years S. R. Mohanty, D. Singh and Gopalkrishna Murthy³ studied the precipitation of zirconium oxalates potentiometrically and reported the formation of four different complexes. But no systematic physico-chemical study has been done on complex formation of zirconium with dicarboxylic acids. The results of the electrometric studies on complex formation of zirconium with oxalic acid and potassium oxalate have been communicated in this paper.

Fig. I



CURVE A: 200 CC. OF $6.25 \times 10^{-3} M, Zr(SO_4)_2 - 0.5 M H_2C_2O_4$.

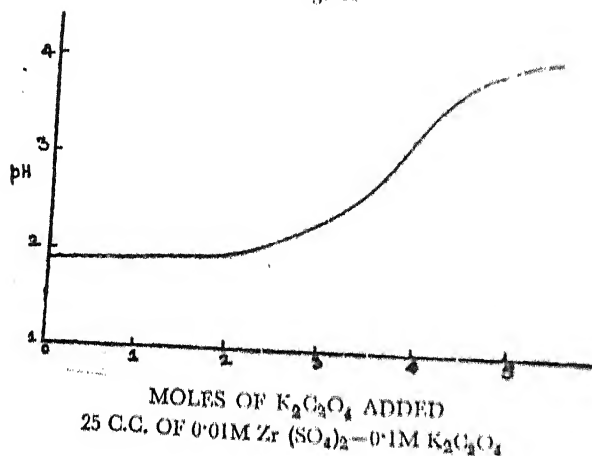
" B: 200 CC. OF $6.25 \times 10^{-3} M, Zr(SO_4)_2 - 0.5 M K_2C_2O_4$.

EXPERIMENTAL

Standard solutions of oxalic acid (A. R.) and potassium oxalate (A. R.) were used. Zirconium sulphate (B. D. H.) solutions were standardised gravimetrically by precipitating with mandelic acid⁴ and igniting the precipitate to oxide. All solutions were made in double distilled water.

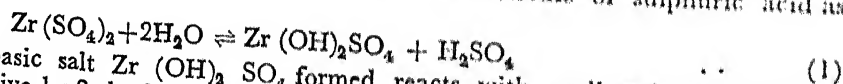
Zirconium sulphate solutions were titrated with oxalic acid and potassium oxalate solutions conductometrically and potentiometrically at $25 \pm 0.1^\circ \text{C}$. on Doran conductivity Bridge and Beckman pH meter model H2. The volume of zirconium sulphate solutions was so large that the effect of dilution on conductance is negligible.

Fig. II



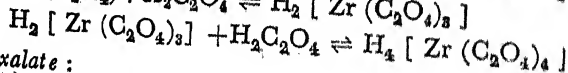
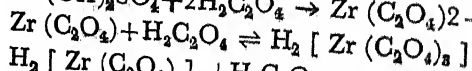
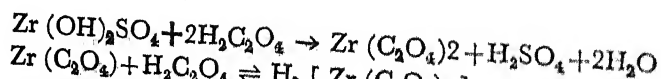
DISCUSSION

It is observed from the conductometric titration curves (Fig. I.) that a sharp break occurs in proportion of 1 : 2, 1 : 3, and 1 : 4 of the reactants. Therefore it can be concluded that the reaction occurs in those proportions. The nature of conductometric titration curves with oxalic acid and potassium oxalate differs considerably. In the former case a rather continuous curve is obtained whereas in the latter case well defined breaks signify the formation of three complexes. It is further observed that addition of oxalic acid or potassium oxalate solution [upto 2 moles), to zirconium sulphate solution produces a white precipitate (zirconium partly precipitated as $\text{Zr}(\text{OX})_2$] which starts redissolving on addition of excess of the reagent to give the second complex with 1 : 3 proportion. The pH of M/100 zirconium sulphate solution was 1.8 indicating the hydrolysis of the salt is over 75 per cent. On hydrolysis it produces one molecule of sulphuric acid as follows :

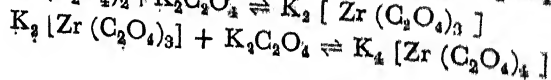
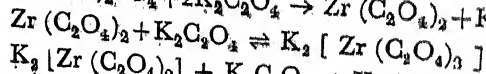
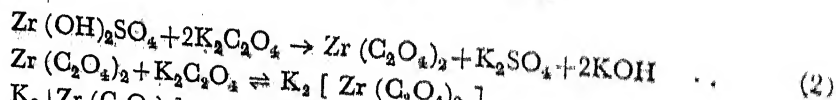


The basic salt $\text{Zr}(\text{OH})_2\text{SO}_4$ formed reacts with oxalic acid or potassium oxalate to give 1 : 2, 1 : 3 and 1 : 4 ratio complexes as follows :

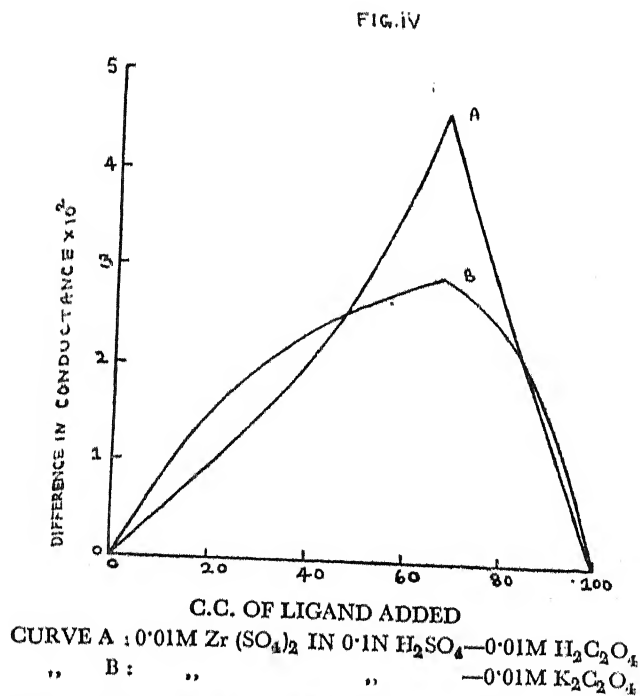
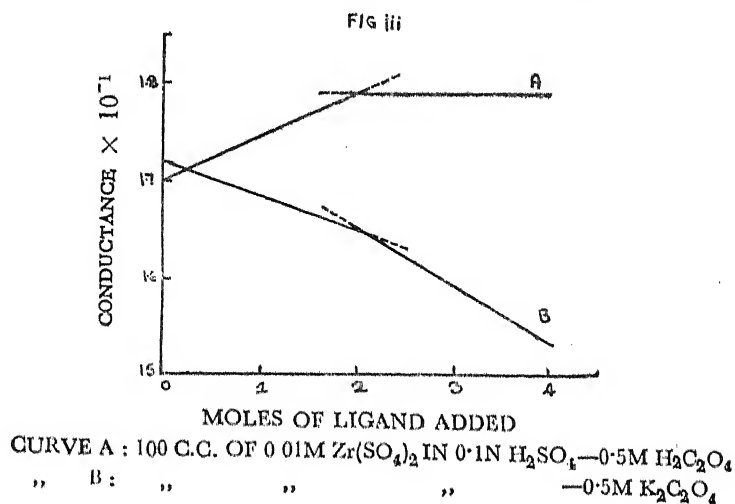
Oxalic acid :



Potassium Oxalate :

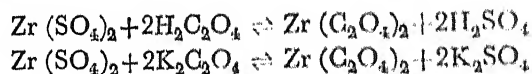


The two molecules of KOH liberated in equation (2) are neutralised by one molecule of H_2SO_4 liberated due to hydrolysis [equation. (1)] hence the pH of the solution remained almost constant upto the formation of 1 : 2 ratio complex with potassium oxalate (Fig. II) The pH titration curve with oxalic acid gives no information because change in pH of the solution is insignificant throughout the titration.



Further we found it to be very interesting to work out the complex formation with the same reagents which gives no precipitate in presence of sulphuric acid. The titration curves are given in Fig. III which show a definite break at 1 : 2 ratio

of the reactions indicating the formation of 1 : 2 ratio complex only. The composition of the complex was also determined by Job's method of Continued Variation.⁵ One set of typical results is represented graphically in Fig. IV. It may be seen from the figure that the peak of the curve occurs at the ratio of 1 : 2 of the reactants. The probable reactions involved in the formation of this complex are :



The presence of sulphuric acid causes no precipitation of $\text{Zr (C}_2\text{O}_4)_2$ which is soluble in sulphuric acid.

ACKNOWLEDGMENT

One of the authors (V. V. S.) wishes to express his thanks to the U. G. C. for the award of a Post-graduate research scholarship.

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STUDY OF COLOUR AND CONSTITUTION OF THE DYES OBTAINED FROM SUCCINIC ACID AND SUBSTITUTED SUCCINIC ACIDS

Part 1.—Dyes from Succinic Acid

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[Received on January 30, 1960]

ABSTRACT

The following succinein dyes have been prepared and their properties studied and their absorption maxima measured :

phloroglucinol succinein, pyrogallol succinein, catechol succinein and quinol succinein.

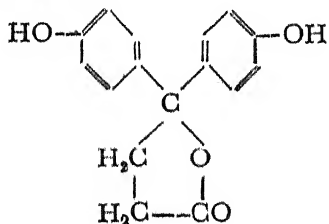
INTRODUCTION

In the present series of investigation an attempt has been made to study the relationship between colour and constitution. Different succinein analogues of phthaleins were prepared by condensing various phenols with succinic acid and substituted succinic acids, and the absorption maxima (λ_{\max}) of these succineins and of the corresponding phthaleins were observed to study the effect produced on the colour of the dye by the replacement of the phthalic acid part in phthaleins by succinic and substituted succinic acids. The structural changes made in the lower portion of phthaleins were of the following kinds :

- (1) The benzenoid phthalic anhydride system was replaced by an aliphatic succinic anhydride system. This change does away with any possibility of conjugation of the central carbon with the lower portion.
- (2) One of the hydrogen atoms of one of the $-\text{CH}_2$ groups of the succinic anhydride part of the succinein was replaced by a phenyl group, thereby the aromatic conjugation was insulated by the intermediary $-\text{CH}_2$ groups.
- (3) In the introduced phenyl group in the succinic anhydride part of the succinein a hydrogen atom of the ring was substituted by a nitro group in the *ortho* and *para* positions and by a chlorine atom in the *ortho* position. These substitutions affected the distance between the two carboxyl groups of the acid and this resulted in the decrement of the yield of the dyes obtained thereof.

We propose to describe first the experimental part relating to the preparation and study of the different series of succinein dyes and then discuss the results and compare them with those of the phthaleins and draw our conclusions. In this first paper of the series the experimental work concerning the preparation and study of succineins is given.

Phenol Succinein,



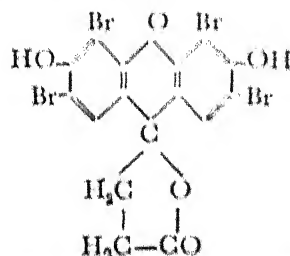
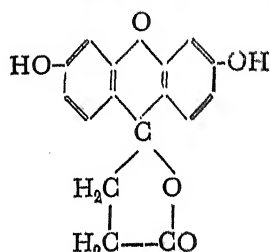
Phenol succinein was prepared according to the method described by Dutt.¹

The dye is almost a colourless solid. It dissolves in alcohol giving a reddish-yellow solution, and in aqueous alkali it dissolves giving a pink solution.

Melting point is 252—253°C. and absorption maximum 5400Å.

Analysis.—Found : C=70.95%, H=5.22% ; the formula $C_{16}H_{11}O_6$ requires C=70.11%, H=5.18%.

Succinyl Fluorescein (Rasorcinol Succinein) and Succinyl Eosin



Succinyl fluorescein and its tetrabromo derivative, succinyl eosin, were prepared according to the method described by Gibbs and Pope²².

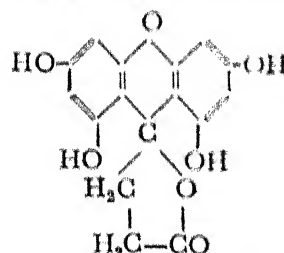
Succinyl fluorescein is dark red in colour. Its alcoholic solution is yellow with a light green fluorescence. In alkali it dissolves giving red solution which on dilution shows intense green fluorescence, the intensity of which appears to be of the same order as that of fluorescein under similar circumstances. The dye melts with decomposition at 234—236°C. Its neutral solution has absorption maximum at 4600Å and its solution having a drop of alkali absorbs at 4800Å.

Analysis.—Found : C=67.58% ; H=4.32% the formula $C_{16}H_{13}O_8$ requires C=67.61%, H=4.22%.

Succinyl Eosin.—It is a brick red solid and dissolves in alcohol giving a red solution. Its solution in dilute alkali is deep red. It melts and simultaneously decomposes at 250—251°C. The dye has absorption maximum at 5400Å.

Analysis.—Found : Br=53.36% ; the formula $C_{16}H_8O_8Br_4$ requires Br=53.33%.

Phloroglucinol Succinein



An intimate mixture of 2.0 gms. of the acid and 6.50 gms. of phloroglucinol was heated in an oil-bath to a temperature of 180°C till it melted. A few drops of concentrated sulphuric acid were then added to the molten mass and the whole mixture stirred well with a glass rod. The temperature was then raised to 200°C and kept there for two hours when the contents of the boiling tube became solid. After cooling, the condensed mass was extracted with dilute sodium hydroxide solution and filtered. From the deep red alkaline filtrate, the dye was precipitated by the gradual addition of dilute hydrochloric acid with constant stirring.

The precipitated dye was filtered under suction, washed with water and dried at 110°C. It was finally purified by crystallisation from alcohol.

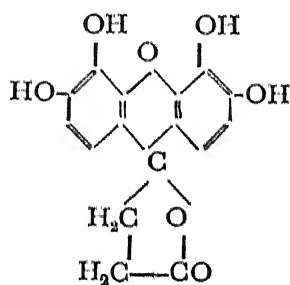
The dye is a brown crystalline solid giving a yellow solution in alcohol. It also dissolves in alkali giving deep red colour. The melting point of the dye is above 300°C, and its absorption maximum 4600Å.

Analysis.—Found : C=60.65%, H=3.81% ; the formula $C_{10}H_{12}O_7$ requires C=60.75%, H=3.79%.

The method adopted for preparing other dyes of this series was almost the same as described above; the conditions under which the reactions were carried out are given below in a tabular form :

Name of the dye	Condensing agent	Temp. C	Duration of heating	Melting point C	λ max.
Pyrogallol succinein	H ₂ SO ₄	160—180°	4 hrs.	above 300°	5400Å
Catechol succinein	„	150—170°	5 hrs.	„	×
Quinol succinein	„	„	„	„	5400Å

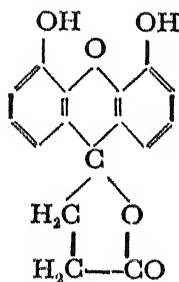
Pyrogallol Succinein,



It is a black solid and dissolves in alcohol giving a slightly green colour. Its solution in alkali is dark and darkens further on keeping.

Analysis : Found : C=60.70%, H=3.85% ; the formula $C_{10}H_{12}O_7$ requires C=60.75%, H=3.79%.

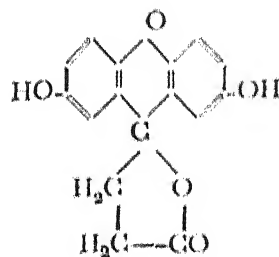
Catechol Succinein,



Catechol succinein is a black solid giving a reddish brown solution in alcohol. In alkali it dissolves giving a dark brown solution.

Analysis.—Found : C=67.58%, H=4.26% ; the formula $C_{16}H_{14}O_5$ requires C=67.61%, H=4.22%.

Quinol Succinein,



Quinol succinein is a black solid giving a light brown solution in alcohol and a dark brown solution in alkali.

Analysis.—Found : C=67.59%, H=4.31% ; the formula $C_{16}H_{14}O_5$ requires C=67.61%, H=4.22%.

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LIQUID CRYSTALLINITY IN SCHIFF'S BASES

By

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ABSTRACT

Some new Schiff's bases have been prepared and their liquid crystalline property has been studied. The liquid crystallinity of these substances has been observed to vary with the polarity of the end groups and an order of group efficiency has been deduced from their mixed liquid crystals with p-azoxy anisole. The order is as under :



Liquid crystalline substances are long rod shaped molecules with polar groups at the centre and the extremities.¹ In fact, the minimum structural requirements have been summarized by Brown and Shaw², and these are satisfied by Schiff's bases. A substance of the type $\text{A} \langle \rangle \text{B} \langle \rangle \text{C}$, where A and C are polar end groups and B a mildly polar central group, should be expected to exhibit liquid crystallinity, which of course has been found to depend upon other factors too. In the case of Schiff's bases, A and C are the different end groups and B the central CH:N group. A number of Schiff's bases, have been prepared and studied in the light of their behaviour for liquid crystallinity, individually, and also in mixtures with another liquid crystalline substance *viz.* p-azoxyanisole. In Table 1 are listed the Schiff's bases with their melting points and transition points, if any.

TABLE I

No.	Schiff's base	M.P.°C	T.P.°C
1.	$\text{O} \cdot \text{CO} \cdot \text{CH}_3 \langle \rangle \text{CH:N} \langle \rangle \text{CH}_3$	99.0	..
2.	$\text{O} \cdot \text{CO} \cdot \text{CH}_3 \langle \rangle \text{CH:N} \langle \rangle \text{Cl}$	110.0	..
3.	$\text{O} \cdot \text{CO} \cdot \text{CH}_3 \langle \rangle \text{CH:N} \langle \rangle \text{OCH}_3$	112.0	119.0
4.	$\text{O} \cdot \text{CO} \cdot \text{CH}_3 \langle \rangle \text{CH:N} \langle \rangle \text{OC}_2\text{H}_5$	118.5	137.5

No.	Schiff's base	M.P.°C	T.P.°C
5.	$\text{O.CO.C}_2\text{H}_5 \langle \text{---} \rangle \text{CH:N} \langle \text{---} \rangle \text{CH}_3$	101.5	(66.4)
6.	$\text{O.CO.C}_2\text{H}_5 \langle \text{---} \rangle \text{CH:N} \langle \text{---} \rangle \text{Cl}$	94.4	(78.3)
7.	$\text{O.CO.C}_2\text{H}_5 \langle \text{---} \rangle \text{CH:N} \langle \text{---} \rangle \text{OCH}_3$	95.0	106.4
8.	$\text{OCH}_3 \langle \text{---} \rangle \text{CH:N} \langle \text{---} \rangle \text{OC}_2\text{H}_5$	128.3	(121.5)
9.	$\text{OCH}_3 \langle \text{---} \rangle \text{CH:N} \langle \text{---} \rangle \text{OCH}_3$	147.0	..
10.	$\text{NO}_2 \langle \text{---} \rangle \text{CH:N} \langle \text{---} \rangle \text{OC}_2\text{H}_5$	123.5	..

A study of Table 1 clearly shows that Nos. 1, 2, 9, and 10 are non liquid crystalline Schiff's bases ; Nos. 5, 6 and 8 are monotropic liquid crystalline Schiff's bases, the isotropic-nematic transition points of which are shown in brackets while Nos. 3, 4 and 7 are enantiotropic liquid crystalline Schiff's bases. In the case of No. 3 the transition points given in the literature⁹ are 112°-128°C, but we find that it definitely melts to a nematic liquid at 112°C, and on further heating it transforms to an isotropic liquid at 119°C; the change from isotropic to nematic (anisotropic) liquid on cooling is also sharp and takes place at 119°C exactly. In the case of compound No. 4 not only there is a higher transition point, but it also possesses a longer phase length. The compound No. 7, *viz.* p-propionoxybenzal-p-anisidine also possesses a greater phase length than the corresponding acetoxy compound No. 3. This can be attributed to the polarity of the groups present in these compounds. It is interesting to note that the p-acetoxybenzal-p-toluidine and p-acetoxybenzal-p-chloroaniline (Nos. 1 and 2) are not only non-liquidcrystalline, but do not exhibit even mono-tropic liquid crystallinity, while the p-propionoxybenzal-p-toluidine and p-propionoxybenzal-p-chloroaniline (Nos. 5 and 6) are both monotropic liquid crystals. This may probably be ascribed to the length and polarity of the propionoxy group compared to that of the acetoxy group.

It should, however, be mentioned that p-anisal-p-phenetidine (No. 8) is a monotropic liquid crystal⁴ while both p-anisal-p-anisidine (No. 9) and p-nitrobenzal-p-phenetidine (No. 10) are non-liquid crystalline Schiff's bases⁶⁻⁷, although p-nitrobenzal-p-phenetidine has a lower melting point and possesses a more polar NO₂ group. It seems, therefore, that the liquid crystallinity in monotropic systems may also depend on other factors like the supercooling and the crystallising tendencies of the compounds.

Binary mixtures of some of the schiff's bases with another liquid crystalline substance *viz.* p-azoxyanisole have been studied, and in tables 2 and 3 are recorded the graphical observations of the study.

The slope of the curve of the transition lines in the case of schiff's bases listed above are given in Table No. 4.

TABLE 2

Solid-liquid transition temperature for the binary system. The eutectic temperatures and m. p. s. of pure components are direct experimental values: the other experimental values are read from the phase diagrams

S. No.	Mole % p-Azoxyanisole (A)											Eutectic	
	0	10	20	30	40	50	60	70	80	90	100	Mole% A	Temp.
1	99.0	94.5	89.5	83.8	85.2	92.5	99.5	105.5	110.3	114.5	118.0	34.5	80.8
2	110.0	106.2	101.2	94.5	87.5	91.7	98.6	105.0	110.5	115.0	118.0	42.0	86.2
5	101.5	97.0	92.2	86.7	86.1	93.8	99.7	105.1	109.5	113.7	118.0	36.0	83.0
6	94.5	90.1	85.5	83.0	84.0	91.1	97.6	103.5	108.8	113.8	118.0	33.2	77.8
8	128.3	123.5	118.5	112.9	106.5	99.0	98.5	104.5	109.5	114.5	118.0	54.5	95.0
9	147.0	143.0	138.5	132.8	126.5	120.0	112.0	105.8	109.5	114.1	118.0	70.5	105.0 ^a
10	123.5	117.5	112.5	107.0	102.0	96.1	95.0	101.5	107.6	113.4	118.0	57.0	93.5

TABLE 3

Isotropic-liquid-nematic liquid transition temperatures. The values are read from phase diagrams

S. No.	Mole % p-Azoxyanisole (A)														Triple-point	
	0	10	20	30	40	50	60	70	75	80	85	90	95	100	Mole %A	Temp.
1	(69.0)	(74.2)	(80.2)	(87.7)	(96.0)	(105.3)	110.0	115.1	120.3	125.5	130.6	136.0	70.5	105.7
2	(98.3)	107.0	111.7	117.0	121.2	126.0	131.0	136.0	63.0	100.7
5	(66.4)	(68.0)	(70.8)	(75.0)	(81.5)	(98.8)	(96.5)	(104.0)	109.0	114.5	120.0	125.5	130.7	136.0	72.1	106.5
6	(78.3)	(78.5)	(79.8)	82.8	87.0	92.5	99.5	107.7	112.2	117.0	121.5	126.0	131.0	136.0	27.0	81.6
8	(121.5)	(120.4)	120.7	121.5	122.5	123.6	125.0	127.1	128.0	129.5	131.0	132.5	134.1	136.0	16.0	102.5
9	119.9	124.0	125.6	128.4	130.0	131.5	133.2	136.0	55.5	116.5 ^a
10	115.2	121.0	125.4	128.6	131.0	132.2	133.1	134.0	134.5	135.4	136.0	23.3	110.5

TABLE 4

S. No.	Schiff's bases	Slope of the curve
1	$\text{O.CO.CH}_3.\text{C}_6\text{H}_4.\text{CH} : \text{N.C}_6\text{H}_4.\text{CH}_3$	10.4
2	$\text{O.CO.CH}_3.\text{C}_6\text{H}_4.\text{CH} : \text{N.C}_6\text{H}_4.\text{Cl}$	10.1
5	$\text{O.CO.C}_2\text{H}_5.\text{C}_6\text{H}_4.\text{CH} : \text{N.C}_6\text{H}_4.\text{CH}_3$	9.8
6	$\text{O.CO.C}_2\text{H}_5.\text{C}_6\text{H}_4.\text{CH} : \text{N.C}_6\text{H}_4.\text{Cl}$	9.5
8	$\text{OCH}_3.\text{C}_6\text{H}_4.\text{CH} : \text{N.C}_6\text{H}_4.\text{OC}_2\text{H}_5$	3.2
9	$\text{OCH}_3.\text{C}_6\text{H}_4.\text{CH} : \text{N.C}_6\text{H}_4.\text{OCH}_3$	4.0
10	$\text{NO}_2.\text{C}_6\text{H}_4.\text{CH} : \text{N.C}_6\text{H}_4.\text{OC}_2\text{H}_5$	1.5

The slope of the curve of the transition line stands as a measure⁷ of the tendency for liquid crystal formation. Further, it has been shown that the group values of the slope of the transition lines are approximately additive and that the values for different end groups can be deduced therefrom. The effect of the central group is either very small or negligible. The table No. 5 gives the values of the end groups arranged in the order of their magnitude.

TABLE 5

OC_2H_5	$>$	OCH_3	$>$	$\text{OCO.C}_2\text{H}_5$	$>$	OCO.CH_3	$>$	CH_3	$=$	Cl
1.0		2.0		2.4		3.05		7.2		7.2

It should be mentioned here that while the slopes of the curve for the group⁸ OCH_3 , OCO.CH_3 and $\text{OCO.C}_2\text{H}_5$ are almost near each other, the p-anisal-p-anisidine (No. 9) is not a liquid crystal⁷ while both p-acetoxybenzal-p-anisidine (No. 3) and p-propionoxybenzal-p-anisidine (No. 7) are genuine enantiotropic liquid crystals. This may probably be due to the lower melting points and the length of the corresponding p-acetoxy and p-propionoxy derivatives as compared to the p-anisal derivative.

EXPERIMENTAL

Preparation and purification of the schiff's bases.—The schiff's bases are prepared by heating equimolar quantities of the corresponding aromatic aldehydes and amines for an hour or two, and recrystallizing the crude product from ethyl-alcohol into fine crystals which melt sharply. The acetoxy and propionoxy derivatives were prepared from the corresponding aldehydes which in turn were prepared from p-hydroxybenzaldehyde by condensing with the respective acid anhydride for two three hours, and distilling the product under vacuum.⁹

p-Acetoxybenzal-p-anisidine, Found N-5.295 %, requires 5.204%, $\text{C}_{16}\text{H}_{15}\text{O}_3\text{N}$.

Method of study.—The phase diagrams are studied by the optical method.⁸

Thanks of the authors are due to Prof. S. M. Sethua for his interest in the work.

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CHEMICAL EXAMINATION OF THE SEEDS OF *CLITORIA MARINA* LINN.

By

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[Received on February 2, 1960]

Clitoria Marina Linn. commonly known as Sweta Aparajita belongs to Papilionaceae sub-group of the Leguminosae family and is distinguished from *Clitoria Ternatea* Linn. by its light blue to almost white flowers. The plant is known for its medicinal properties¹ and the flowers find use in the treatment of cramps and paralysis². Although studies have been carried out on the plant *Clitoria Ternatea* Linn. by Tewari and Gupta,³ a survey of literature reveals that no systematic chemical examination has been reported so far on any part of the plant *Clitoria Marina* Linn. A systematic chemical examination of the seeds of this plant has been carried out and the findings have been reported in the present communication.

EXPERIMENTAL

The plant *Clitoria Marina* Linn. was specially grown for purposes of chemical examination from authentic specimen of seeds and distinguished by its light blue to almost white flowers. The ripe large seeds were collected and sun-dried.

Powdered seeds on complete incineration in a muffle furnace at 600° for 3 hours left a white ash (yield 2.36%) of which 38.8% was water soluble and the rest acid soluble. The ash on analysis was found to contain sodium, potassium, calcium, magnesium, iron and aluminium as the basic radicles and chloride, sulphate and phosphate as the acid radicles. By the application of flame photometric and colorimetric techniques, the amounts of sodium, potassium, calcium, magnesium, iron and aluminium have been found to be 318.6, 923.5, 198.5, 190.0, 20.8 and 15.0 mg. respectively per 100 g. of the seeds on dry weight basis.

The powdered seeds were extracted with a number of solvents in succession in an all glass soxhlet with 3 vols. of the solvent for 20 hours in each case and the yield and characteristics of the extracts have been given below in Table 1.

TABLE 1
Showing solubility characteristics of the seeds

Sl. No.	Solvent	% yield	Characteristics
1	Petroleym ether (b.p. 40°-60°)	18.5	The extract was pale yellow in colour and consisted of a fixed oil.
2	Solvent ether	14.5	As above but in lower yield.
3	Chloroform	1.8	An yellowish-green resinous mass was obtained.
4	Absolute alcohol	2.4	An yellowish-green sticky residue was obtained.
5	75% alcohol	2.1	As above but in lower yield.

The aqueous extract of the seeds gave positive tests for reducing sugars and tannins but saponins and alkaloids were found to be absent. The seeds on examination were found to contain the following constituents.

Shell	..	11.2	per cent.
Kernel	..	88.8	per cent.
Ash	..	2.36	per cent.
Moisture	..	4.3	per cent.
Reducing sugars	..	2.5	per cent.
Fibrous material	..	2.0	per cent.
Nitrogen content	..	1.0	per cent.

Examination of the oil.—The fatty oil obtained in 18.5% yield by extracting the powdered seeds (2 Kg.) after careful decortication with petroleum ether (b.p. 40°—60°) and evaporation of the solvent was bright yellow in colour. The oil was purified by repeated treatment with animal charcoal and Fuller's earth. It was non-drying and possessed the following characteristics :

Specific gravity at 30°	..	0.9182
Refractive index at 30°	..	1.4630
Acid Value	..	10.5300
Acetyl Value	..	18.0000
Saponification Value	..	186.8000
Iodine Value (Hanus)	..	118.0000
R. M. Value	..	0.3000
Hehner Number	..	84.7600
Thiocyanogen Value	..	82.6500
Unsataponifiable Matter%	..	1.6000

Examination of fatty acids.—The oil (100 g.) was saponified in the usual manner, the unsaponifiable matter extracted with ether and the fatty acids were liberated by treatment of the soap with dil. H_2SO_4 . The mixed acids were separated into saturated and unsaturated acids by Twitchell's lead salt alcohol process as modified by Hilditch.⁴ The liberated acids possessed the following properties :

TABLE 2
Showing the properties of the liberated acids

Serial No.	Name of acid fraction	% yield	Iodine value	Thiocyanogen value	Neutral value	Mean Mol. wt.
1.	Mixed acids	—	118.0	82.65	182.5	273.6
2.	Solid acids	20.0	5.0	3.50	183.8	268.8
3.	Liquid acids	80.0	136.5	84.50	185.0	275.6

Examination of unsaturated acids.—The liquid acids were oxidised with dil. $KMnO_4$ solution according to the method of Lapworth and Mottram⁵, when a dihydroxy stearic acid, m. p. 132° and a tetrahydroxy acid, m.p. 177° were obtained showing the presence of oleic and linoleic acids. The percentages of oleic and linoleic acids were determined by bromination of the liquid acids in ethereal solution at —10° according to the method of Muggenthaler⁶ as modified by Jamieson and Boughman⁷ and were found to be 51.7 and 15.6 % respectively in the mixed acids.

Examination of saturated acids.—The saturated acids were converted into their methyl esters and the mixed esters fractionally distilled under reduced pressure. The saponification value of these fractions were determined. The acids were then liberated from the the different fractrons and characterised by their melting points after fractional crystallisation and from the melting points of their amide and anilide derivatives, prepared in the usual manner. The quantities of the various acids in these fractions were calculated according to the method of Jamieson and Boughman⁷ and have been shown below in Table 3.

TABLE 3
Showing percentage composition and characteristics of the acids

Serial No.	Name of acid	m. p. of acid in °C	b. p. of methyl ester in °C mm	m. p. of anilide in °C	m. p. of amide in °C	% in saturated acid	% in mixed acid
1.	Myristic	54°	110/1	79	100	9.0	1.8
2.	Palmitic	63°	130/1	90	105	44.0	8.8
3.	Stearic	70°	155/1	94	110	16.5	3.3
4.	Archidic	75°	180/1	97	107	5.0	1.0

Examination of unsaponifiable matter.—The unsaponifiable matter obtained on removal of ether was examined and a crude sterol fraction was isolated from it. From this fraction, the pure sterol has been obtained by repeated crystallisation of the corresponding acetates and benzoates and by chromatography of the product over Brockman alumina column. The sterol has been identified as γ -sitosterol.

Examination of reducing sugars.—The seeds contained 2.5% of reducing sugars which were identified as arabinose, xylose and rhamnose by paper chromatography by the procedure described earlier by the author^{8,9}.

SUMMARY

The seeds of *Clitoria Marina* Linn. have been examined and found to contain 18.5% of a fixed oil. The component fatty acids of the oil have been found to be oleic 51.7, linoleic 15.6, myristic 1.8, palmitic 8.8, stearic 3.3 and archidic 1.0% respectively. The unsaponifiable matter consisted of γ -sitosterol.

ACKNOWLEDGMENT

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CHEMICAL EXAMINATION OF THE MUCILAGE FROM THE LEAVES AND COLOURING MATTERS FROM THE FLOWERS OF *CLITORIA MARINA* LINN.

By

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The mucilage from the leaves of *Clitoria marina* Linn. has been obtained as a white powder by precipitation with alcohol. It was non-reducing having $[\alpha]_D^{25} +20.0$ (c, 2% in water) and showed the presence of 71.5, 12.4 and 8.0% of anhydrogalactan, anhydropentosan, and methyl pentosan respectively. Mild hydrolysis of the mucilage with 10% sulphuric acid showed the presence of D-galactose, L-arabinose and rhamnose. The purified mucilage on methylation gave a methylated product [OMe , 38.0%; $[\alpha]_D^{25} -41.0$ (c, 2% chloroform)]. The methylated product on hydrolysis indicated the presence of two sugars, one of which has been identified as tetra O-methyl galactose.

The colouring matter has been isolated from the flowers by exhaustive extraction with 70% alcohol. From the crude residue, two fractions of acetone soluble matter has been separated by column chromatography. The characteristics of the isolated colouring matter has been investigated and the product has been found to be a glucoside containing two methoxy groups. The aglycone fraction, $\text{C}_{30}\text{H}_{36}\text{O}_6$ has been found to contain two methoxy and three hydroxy groups.

Clitoria marina Linn., commonly known as *Sweet aparajita* belongs to *Papilionaceae* sub-group of the *Leguminosae* family and is distinguished from *Clitoria ternatea* Linn. by its light blue to almost white flowers. The plant is known for its medicinal properties¹ and the flowers find use in the treatment of cramps and paralysis². Although investigations have been carried out on the leaves of the plant *Clitoria ternatea* Linn. by Tewari and Gupta³, a survey of available literature reveals that no systematic chemical examination has been reported so far on any part of the plant *Clitoria marina* Linn. A preliminary examination of the leaves showed the presence of an essential oil, colouring matters and mucilage besides a δ -lactone compound. In the present communication, studies on the mucilage obtained from the leaves and the colouring matter contained in the flowers have been reported.

EXPERIMENTAL

The plant *Clitoria marina* Linn. was specially grown for purposes of chemical examination from authentic specimen of seeds and distinguished by its light blue to almost white flowers. The leaves and flowers were collected and sun-dried.

INVESTIGATIONS ON THE MUCILAGE

Isolation and purification of mucilage

1.0 Kg. of dried and powdered leaves were exhaustively extracted with petroleum ether (b.p. $40^\circ\text{--}60^\circ$) and acetone to remove oil, colouring matters and other impurities. The residue was then allowed to soak in a litre of 5% acetic acid at 25° for 24 hours. The product was then mechanically stirred for 12 hours and filtered through glass wool. The filtrate was then mixed with an excess of absolute alcohol, the product agitated when a sticky mass was obtained (yield 7.5%). The

crude mucilage was dissolved by boiling in 5% acetic acid solution and filtered. The filtrate was mixed with absolute alcohol and the mixture stirred as before when the mucilage was precipitated out. It was dried and successively refluxed with petroleum ether, ether, benzene, chloroform and absolute alcohol to remove all other organic impurities. Finally, it was dried in vacuum.

The mucilage was found to be a neutral polysaccharide and did not possess acetyl or methoxy groups. On complete incineration in a muffle furnace, it left a white ash (yield 1.2%). The nitrogen content was found to be 0.6%.

The pure mucilage free from ash and nitrogen has been obtained as a white powder by Fraenkel and Jellineck's procedure⁴. The purified mucilage was non-reducing having $[\alpha]_D^{25} + 200.0$ (c, 2% in water). It gave positive tests for galactan, pentosan and methyl pentosan and negative tests for ketoses and uronic acid. Pentoses and methyl pentoses were estimated by A. O. A. C. methods while galactose was estimated by hydrolysing the mucilage and preparing galactose α -methyl phenyl hydrazone by Hirst, Jones and Woods method⁵. The quantitative estimation of the sugars showed the presence of 71.5, 12.4 and 8.0% of anhydrogalactan, anhydropentosan and methyl pentosan respectively. The mol. wt. of the pure mucilage was found to be 1240 (cryoscopically). The viscosity of the gelatinous solution of the mucilage was determined at pH 3.0, 4.0, 4.5, 5.0, 5.5 and 6.0 by Ostwald Viscometer at 25° and was found to be 2.3, 2.6, 2.8, 3.0, 3.8 and 3.6 centipoise respectively. The viscosity increased with rising pH and the maximum value was noted at pH 5.5. On ageing the solution, the viscosity decreased rapidly.

Hydrolysis of mucilage with 10% sulphuric acid

The pure mucilage (5.0 g.) was completely hydrolysed by heating with 100 c.c. of 10% H_2SO_4 on a water bath. The hydrolysis was followed polarimetrically as well as by determining the reducing power of the hydrolysate from time to time and was complete in 6 hours. The hydrolysate was neutralised with $BaCO_3$ and concentrated to a syrup under reduced pressure. This solution on chromatographic examination⁶ was found to contain three sugars. The syrup on extraction with dry methyl alcohol left a residue which was subsequently identified as galactose. The residue on crystallisation gave pure crystalline D-galactose, m. p. 164°, $[\alpha]_D^{25} + 800.0$ (c, 2% in water). There was no depression of m. p. when mixed with an authentic specimen of D-galactose. The methyl alcohol extract on concentration deposited white crystals of L-arabinose, which were subsequently crystallised twice from dry methyl alcohol, m. p. and mixed m. p. with an authentic specimen, 158°, $[\alpha]_D^{25} + 1050.0$ (c, 2% in water). Its phenyl hydrazone, prepared as usual, melted at 201°. The mother liquor left after separating L-arabinose gave positive Rosenthaler's test and the R_f value was identical with that of rhamnose.

Mild hydrolysis of the mucilage with 10% H_2SO_4 under the conditions stated by White⁷ so as to hydrolyse the pentoses in furanose form only failed to effect the complete rapture of arabinose from the mucilage. This indicates that at least some part of arabinose must be present in the pyranose form.

Preparation of methylated mucilage

The mucilage (5 g.) was methylated four times at 25° by adding dimethyl sulphate (75 c. c.) and 30% NaOH (200 c. c.) each time during 8 hours and concentrating the solution to remove Na_2SO_4 . The product was dissolved in acetone

and re-methylated three times by the above procedure. The partially methylated product was then dissolved in chloroform, washed with 20% NaOH and finally dried over fused Na_2SO_4 . The extract on removal of solvent left a residue (yield 4.5 g.; OMe 32%). The product was finally again methylated twice by Purdie's reagent⁸ when a methylated product [OMe , 38%, $[\alpha]_{\text{D}}^{25} - 11.0$ (c, 2% CHCl_3)] was obtained. Further treatment with Purdie's reagent did not increase the methoxy content (yield 4 g.)

Hydrolysis of methylated mucilage

1.0 g. of the methylated mucilage was heated with 60 c. c. of 7% HCl—methyl alcohol mixture in a sealed tube for 6 hours at 90° . It was diluted with 60 c. c. of N. HCl and again heated at 90° for 3 hours. The hydrolysate was treated with silver carbonate, filtered and the filtrate treated with H_2S to remove silver ions and again filtered. The filtrate was concentrated to a syrup under reduced pressure and indicated the presence of two sugars on chromatographic examination. The two sugar fractions were separated on a cellulose column 80×4 cm. using benzene-ethyl alcohol-water (11:3:1, v/v) as the eluting mixture. The two fractions were collected and were found to be 52 and 8% respectively of the syrup.

Identification of 2:3:4:6 tetra-O-methyl D-galactose

The syrup was found to have 46% methoxy content and optical rotation $[\alpha]_{\text{D}}^{25} + 60.0$ (c, 2% in ethyl alcohol). On chromatographic examination and comparison against authentic specimen in control chromatograms, the sugar was identified as 2:3:4:6 tetra-O-methyl D-galactose ($\text{C}_{10}\text{H}_{20}\text{O}_6$ requires OMe, 52.1%; optical rotation $[\alpha]_{\text{D}}^{27} + 62.6$ (c, ethyl alcohol)⁹. It was further confirmed by preparing its anilide, m. p. and mixed m. p. 194° . (Found: OMe, 39.4%. Calc. for $\text{C}_{18}\text{H}_{25}\text{O}_6$, N: OMe, 39.9%). The other sugar fraction constituting 8% of the syrup could not be examined as it was insufficient.

The low mol. wt. (1240) of the mucilage suggests that the methyl pentose present may not be the constituent of the polysaccharide molecule. The relatively larger proportion of galactose molecule and its derivatives suggests that the mucilage contains a highly branched chain with 1:2 and 1:3 linkages. The optical rotations of the mucilage and its methylated product suggest β -linkages.

INVESTIGATIONS ON COLOURING MATTER

Extraction of colouring matter

1 Kg. of sun-dried and powdered flowers of *Clitoria marina* Linn. were exhaustively extracted with 70% alcohol in a all glass soxhlet for 16 hours. The product was filtered hot and the filtrate cooled and kept at 10° for 10 hours when no solid substance separated. The extract was then concentrated to a syrupy mass under reduced pressure. The water soluble constituents of the syrupy mass were removed by boiling with water for an hour. It was filtered and the residue was treated with 100 c. c. of 0.5 N. NaOH, the product agitated and filtered. The filtrate was acidified with dil. HCl when a ppt. was formed. The ppt. was washed with water, dried and refluxed with acetone on a water bath for 2 hours. The reaction product was cooled, filtered and washed with acetone. The residue was dried in a vacuum desiccator and the filtrate containing acetone soluble substance collected.

Examination of acetone soluble portion

The residue obtained on distilling off the acetone filtrate was purified by dissolving the crude product in ether and by mixing the ether extract with excess of benzene, when a ppt. was obtained. It was filtered, washed with benzene, dried and recrystallised from acetone. The substance was separated into two fractions on a cellulose column using methyl alcohol and water (7:2, v/v) and ethyl acetate and ethyl alcohol (8:2, v/v) as the successive eluting mixtures. The first fraction contained 90% and the second 10% of the colouring matter, the latter being insufficient for further work. The first fraction contained C, 65.92; H, 6.95%; M. W. 660; OMe, 9.5%. Calc. for $C_{36}H_{46}O_{11}$: C, 66.18; H, 7.03%; M. W. 654; 2 OMe 9.5%.

Characteristics of the colouring matter

The colouring matter was soluble in alcohol, acetone, ethyl acetate and ether and insoluble in petroleum ether, benzene and chloroform. It gave a bluish violet colour with ferric chloride in alcohol, a pink colour with NaOH changing to yellow on addition of dil. HCl and a red colour with conc. H_2SO_4 . Free carboxyl groups were found to be absent. It reduced Fehling's solution. On hydrolysis and subsequent neutralisation, the filtrate continued to reduce while the residue did not reduce the Fehling's solution, indicating thereby that the colouring matter was glucosidic in nature. It also decolourised alkaline $KMnO_4$ solution and bromine water.

Hydrolysis of the colouring matter

1 g. of the colouring matter was refluxed with 50 c. c. of 10% HCl for 6 hours. The reaction product was filtered and the filtrate kept for sugar analysis. The insoluble aglycone residue was washed with water, dissolved in absolute alcohol and crystallised.

Examination of sugar component

The filtrate obtained on hydrolysis of the colouring matter was neutralised with dil. NaOH and concentrated to a syrup under reduced pressure. It was then extracted with methyl alcohol, shaken and filtered. The residue was dissolved in water and the solution on chromatographic examination showed the presence of glucose.

Examination of aglycone residue

The aglycone residue was analysed. Found: C, 73.06; H, 7.25; OMe, 12.2%; M. W. 500. Calc. for $C_{30}H_{36}O_6$: C, 73.17; H, 7.32; 2 OMe, 12.6%; M. W. 492. The tri-acetyl derivative of the substance was prepared in the usual manner. Found: OAc, 20.8%; M. W. 620. Calc. for $C_{36}H_{42}O_9$: 3 OAc, 20.88%; M. W. 618.

Examination of acetone insoluble portion

The acetone insoluble portion of the colouring matter was separated into two fractions by column chromatography using alcohol-benzene-water (2:7:1, v/v), benzene-ether (1:1) and absolute alcohol as the successive eluting mixtures. The quantities of these two fractions obtained from the first two solvents were insufficient for further work.

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ON THE BOUNDEDNESS OF SOLUTIONS OF NON-LINEAR DIFFERENTIAL SYSTEMS

By

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This is a continuation of the author's work^{1,2} in this field. In this note some results for the boundedness of solutions of non-linear differential systems are derived under a set of more liberal conditions. Our discussion depends on the following simple lemma proved in.¹ It will be stated here in a different form so as to suit our purpose.

1. Lemma: Let the function $y(x)$ be continuous on $x_0 \leq x < \infty$ and satisfy the inequality

$$y'(x) \leq h(x, y(x)) \quad (1)$$

where the function $h(x, r)$ is continuous in the domain $x_0 \leq x < \infty, r \geq 0$. Then

$$y(x) \leq r(x) \quad \text{for } x_0 \leq x < \infty. \quad (2)$$

where $r(x)$ is the maximal solution of $r' = h(x, r)$, $r(x_0) = y(x_0)$.

(2). Let y and $f(x, y)$ be vectors with real components (y_1, y_2, \dots, y_n) and $(f_1(x, y), f_2(x, y), \dots, f_n(x, y))$ respectively. Define $x \cdot y = x_1 y_1 + x_2 y_2 + \dots + x_n y_n$. Consider the system

$$y' = f(x, y), \quad y(x_0) = y_0 \quad (3)$$

where the function $f(x, y)$ is continuous on $x_0 \leq x < \infty, |y| < \infty$, and y_0 is a vector. Then we have

Theorem 1. Suppose that the function $h(x, r) \geq 0$ is continuous on $x_0 \leq x < \infty, r \geq 0$ and that

$$y \cdot f(x, y) \leq -h(x, y \cdot y) \quad (4)$$

Then each component of every solution $y(x)$ of (3) tends to a finite limit as $x \rightarrow \infty$.

An additional restriction gives the following:

Theorem 2. Suppose that the conditions of theorem 1 hold.

Suppose further that the maximal solution $m(x)$ of $r' = -2h(x, r)$, $m(x_0) = y_0 \cdot y_0$ satisfies $m(x) = o(1)$ as $x \rightarrow \infty$. Then each component of every solution $y(x)$ of (3) tends to zero as $x \rightarrow \infty$.

Proof of theorem 1. Let $y(x)$ be the solution of (3). Write $r(x) = y(x) \cdot y(x)$. Then it follows that $r'(x) = 2y(x) \cdot f(x, y(x))$.

Hence using the condition (4), we obtain

$$r'(x) \leq -2h(x, r(x)). \quad (5)$$

It is clear from (5) that the derivative of $r(x)$ is non-positive. Consequently $r(x)$ is non-increasing as x increases from $x = x_0$. It is also seen that $r(x)$ tends to finite limit as $x \rightarrow \infty$. Hence the stated result follows.

To prove theorem 2, we have to proceed from (5). Using the lemma stated above, we get from (5) that

$$r(x) \leq m(x) \text{ for } x_0 \leq x < \infty, \quad (6)$$

where $m(x)$ is the maximal solution of $r' = -2h(x, r)$, $m(x_0) = r(x_0)$. The inequality (6) together with the assumptions of the theorem yield the stated result.

It is easy to extend the above results to compare the solutions of two differential systems. Let z and $g(x, z)$ be vectors with real components (z_1, z_2, \dots, z_n) , $(g_1(x, z), g_2(x, z), \dots, g_n(x, z))$. Consider the system

$$z' = g(x, z), \quad z(x_0) = z_0 \quad (7)$$

where $g(x, z)$ is continuous on the region $x_0 \leq x < \infty$, $|z| < \infty$. Then we have the following comparison

Theorem 3. Suppose that the function $h(x, r) \geq 0$ is continuous on $x_0 \leq x < \infty$, $r \geq 0$ and that the functions $f(x, y)$ and $g(x, z)$ satisfy the condition

$$(y-z) \cdot (f(x, y) - g(x, z)) \leq -h(x, (y-z) \cdot (y-z)) \quad (8)$$

Then each component of every solution of (3) and (7) tends to a finite limit as $x \rightarrow \infty$.

If further the maximal solution $r(x)$ of $r' = -2h(x, r)$, $r(x_0) = r_0$ is such that $r(x) = o(1)$ as $x \rightarrow \infty$, then each component of every solution $y(x)$ of (3) tends to the same finite limit, as that of the corresponding component of every solution $z(x)$ of (7), as $x \rightarrow \infty$.

Corollary: If $g(x, z) = 0$, the above result reduces to theorems 1 and 2 and hence it is more general.

The proof of theorem (3) is similar to that of theorems 1 and 2; hence omitted.

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THE BRIGHT PLATINUM ELECTRODE

By

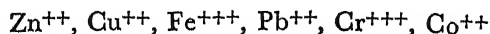
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ABSTRACT

It is possible to titrate acids with sodium hydroxide accurately using a bright platinum electrode, no bubbling of hydrogen or addition of quinhydrone being necessary. In the same way the quantitative precipitation of



and perhaps some other metal ions with NaOH can be followed. In these titrations the system probably works as an oxygen electrode,



Hence it works indirectly as a hydrogen electrode. Complex formation between ferric ions and fluoride, acetate, propionate, tartrate or citrate ions as well as bromination of phenols and aromatic amines can be followed equally successfully. In these cases the electrode may work as a redox indicator, its function as an oxygen electrode having been suppressed. The electrode may also be used for pH measurements in the range 3-9 with moderate accuracy. Its behaviour under different treatments has been briefly discussed.

INTRODUCTORY

The bright platinum electrode is commonly used as a redox indicator. Thus, it can be used for following the equilibrium of quinhydrone with hydrogen ions or that of ferric ions with ferrous ions. If a trace of ferrous ions is introduced into a ferric chloride solution, theoretically it should be possible to titrate the ferric ions with a wide variety of reagents *e.g.* NaOH or NaF, since ferric ions will be continuously removed changing the ferric/ferrous ratio. So also, if the platinum has previously come in contact with a flame a possibility exists that it may have adsorbed a trace of hydrogen formed in the thermal decompositions, and held the gas sufficiently tenaciously to act as a hydrogen electrode. It may then be possible to titrate a mineral acid, for example, with an alkali without platinizing or bubbling hydrogen.

Preliminary experiments showed that both these latter titrations (ferric chloride or mineral acids with NaOH) can be successfully carried out. In the titration of ferric chloride with NaOH not only is the ferric/ferrous ratio changing but also the concentration of H^+ ions. It is therefore not quite clear whether the bright platinum in this titration is functioning as a hydrogen electrode or simply as an inert electrode capable of following the ferric/ferrous ratio. Obviously, potentials corresponding to both must be set up, but one of them perhaps preponderates over the other in an experimental sense. A theoretical discussion of such electrode systems may not be easy, but the existence of steep inflexions in titrations at the correct end point clearly indicates that whatever the values of the corresponding E_0 's and whatever their significance in some cases at least they are sufficiently steady during a titrations to merit further experimental study. We were thus led to carry out the titrations described below. Some pH measurements were also made with encouraging results.

EXPERIMENTAL

A platinum foil electrode one cm square was selected for these titrations. The foil was cleaned in hot chromic acid, washed, dried and polished with a rounded glass rod. It was then glowed in a wickless flame of methyl or ethyl alcohol. For this purpose the alcohol was taken in a small porcelain basin and ignited. Several other organic substances (ether, acetone) were tried, but the most reproducible behaviour of the electrodes was observed with the two alcohols. 10 cc of the solution to be titrated was taken in a beaker or small bottle, the electrode fully immersed and the titration carried out with the appropriate solution usually about normal in strength. A saturated calomel was used as the other half cell and potentials were measured on a simple stretched wire potentiometer with an accuracy of one millivolt.

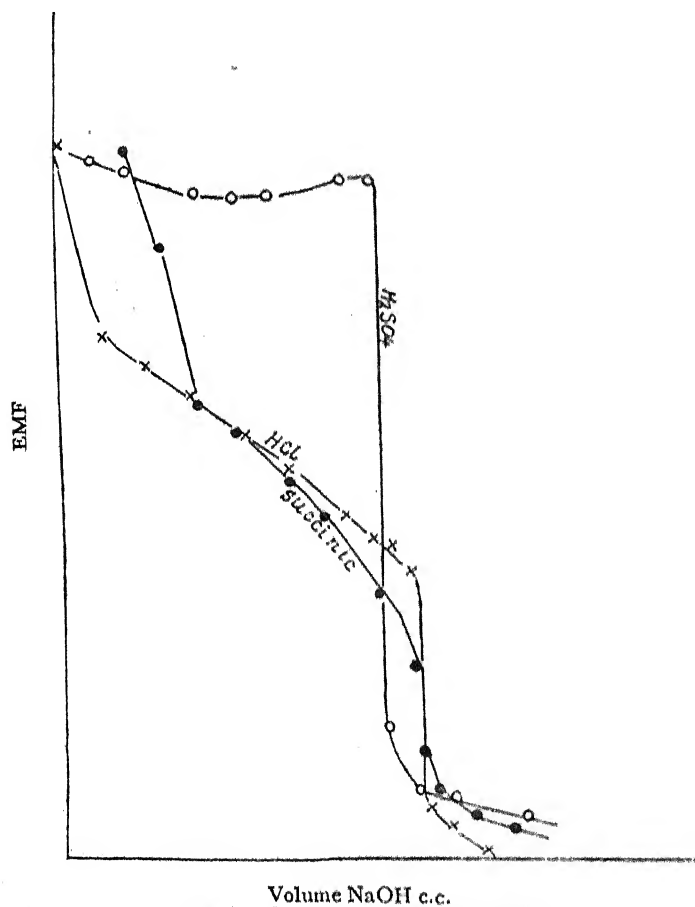


Fig. 1. Titration of acids with NaOH

The titration graphs (EMF against volume delivered) in many cases show an unexpectedly steep inflexion capable of extrapolation without the least uncertainty. Some of the results are shown in Figs. 1-4. Some relevant data concerning these titrations are given in Table 1.

TABLE 1
Titrations with bright platinum electrode

1. Mineral Acids and NaOH

Cell	Burette, approx. strength.	found, cc.	expected, cc.
10 cc N/10 NaOH	N/1 HNO ₃	0.805	0.805
10 cc N/10 HCl	N/4 HaOH	4.00	3.95
10 cc N/25 H ₂ SO ₄	N/4 NaOH	1.80	1.80
10 cc N/10 Succinic Acid	N/1 NaOH	0.801	0.805
10 cc N/10 Ac. Acid.	N/1 NaOH	0.801	0.805

2. Ferric Chloride and Complexing Agents.

Cell, app. Conc.	Burette, app. conc.	found, cc.	expected, cc.
10 cc N/10 FeCl ₃	N/10 Na-acetate	9.10	9.10
10 cc N/10 FeCl ₃	N/10 Na-propionate	9.20	9.10
10 cc N/10 FeCl ₃	N/10 Na-citrate	12.60	12.60
10 cc N/10 FeCl ₃	N/10 Na-tartrate	8.20	8.20
10 cc N/10 FeCl ₃	N/10 Na-fluoride	6.00	9.10

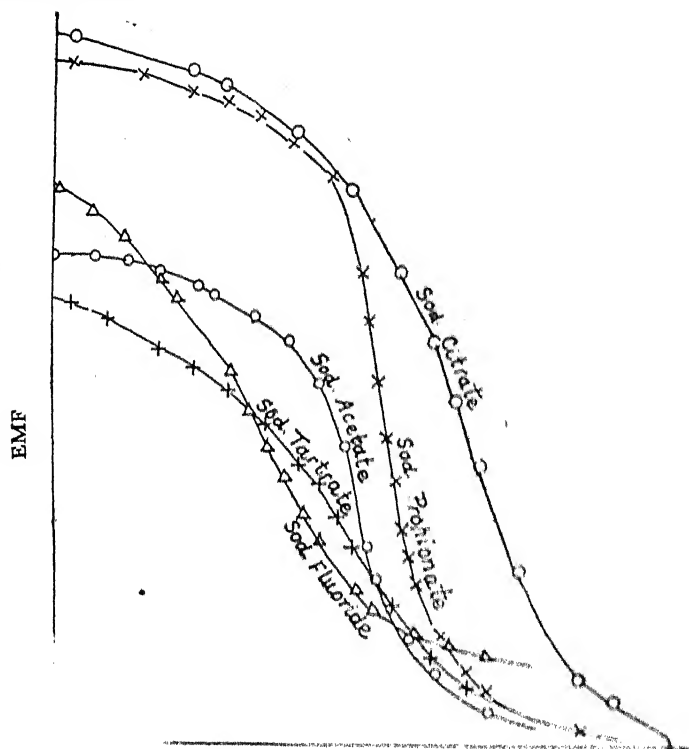
3. Precipitation with NaOH

10 cc .099 N FeCl ₃	.979 N NaOH	1.07	1.09
10 cc .099 N FeCl ₃	.484 N NaOH	2.05	2.04
10 cc .099 N FeCl ₃	.161 N NaOH	5.95	6.10
10 cc .100 N ZnSO ₄	1.189 N NaOH	0.80	0.84
10 cc .100 N CuSO ₄	1.189 N NaOH	0.80	0.84
10 cc .100 N Pb (NO ₃) ₂	.979 N NaOH	1.04	1.02
10 cc .092 N CoCl ₂	.979 N NaOH	0.96	0.93
10 cc .111 N MnSO ₄	1.189 N NaOH	0.95	0.93
(with pinch of MnO ₂)			
10 cc .111 N MnSO ₄	1.189 N NaOH	0.95	0.93
(with a drop of KMnO ₄)			
10 cc .100 N CdSO ₄	1.189 N NaOH	0.70	0.84

4. Bromination of Organic Substances.

10 cc .100 M phenol	1.667 M bromate	5.90	6.00
10 cc .100 M aniline	"	6.00	6.00
10 cc .100 M resorcinol	"	6.00	6.00
10 cc .100 M p-nitraniline	"	3.90	4.00
10 cc .100 M m-phenylene diamine	"	4.10	4.00
10 cc .100 M toluidine in HCl	"	4.10	4.00
10 cc .100 M thymol	"	2.90	3.00?

The successful acid-alkali titrations as well as precipitations with NaOH show that the bright platinum electrode can act as a hydrogen electrode with a steady E_0 . In the titrations of ferric chloride with complex forming agents, however, the electrodes must be following the ferric/ferrous ratio. It was not necessary to add external ferrous ions. It seems that enough ferrous ions are always present in solutions of ferric salts for a successful titration. These ferrous ions may perhaps be produced by photochemical reduction or reduction by traces of organic substances invariably present.



Volume complexing agent c.c.
Fig. 2. Titration of FeCl_3 with complexing agents

The successful titration of phenols and amines with bromine is curious. The bromo-compounds formed are all insoluble. The electrode potential at any stage probably corresponds to equilibrium of the type, $\text{C}_6\text{H}_5\text{OH} + 3\text{Br}_2 \rightleftharpoons \text{C}_6\text{H}_2\text{Br}_3\text{OH} + 3\text{HBr}$, i.e., to the ratio $\text{C}_6\text{H}_2\text{Br}_3\text{OH}/\text{C}_6\text{H}_5\text{OH}$, and to that extent the working of the electrode is perhaps akin to that of the quinhydrone electrode, i.e., a redox electrode.

It will be noted that some results recorded in the above Table are anomalous and require re-examination, e.g., the titrations of CdSO_4 and thymol. Subsequently, a number of mixtures were also prepared containing a salt and an acid e.g., ferric chloride-sulphuric acid. Sharp end points were obtained for each on titration with NaOH. When CuSO_4 was titrated with a more dilute NaOH (N/10) a steep inflexion corresponding to a basic salt appeared before the final inflexion corresponding to $\text{Cu}(\text{OH})_2$. There was a similar indication in the case of MgSO_4 . Ferric chloride or zinc sulphate did not show any such behaviour.

DISCUSSION

It is quite clear therefore that the function of the bright platinum depends upon the prevailing conditions in the solution. It may function as a simple redox indicator or a hydrogen electrode directly or indirectly. In this connection it is necessary to point out some cases in which a titration failed completely, namely, those of FeSO_4 , NiSO_4 , BaCl_2 and MnSO_4 in absence of MnO_2 or KMnO_4 . Among these the last case is comparatively easy to understand. In the absence of MnO_2 or KMnO_4 , the platinum can function only as a hydrogen electrode (see below) but the presence of manganous ions makes this function impossible due to some reason or other. In fact the titration graphs show a large drop of potential with the first few drops of NaOH added. Such a behaviour is to be expected if a trace of Mn^{+++} ions, for example, is present in the solution. The first few drops of NaOH will remove manganic ions completely, producing at the same time a large drop in potential. The subsequent changes in potential on continuing the titration are too meagre to be useful for detecting the end point.

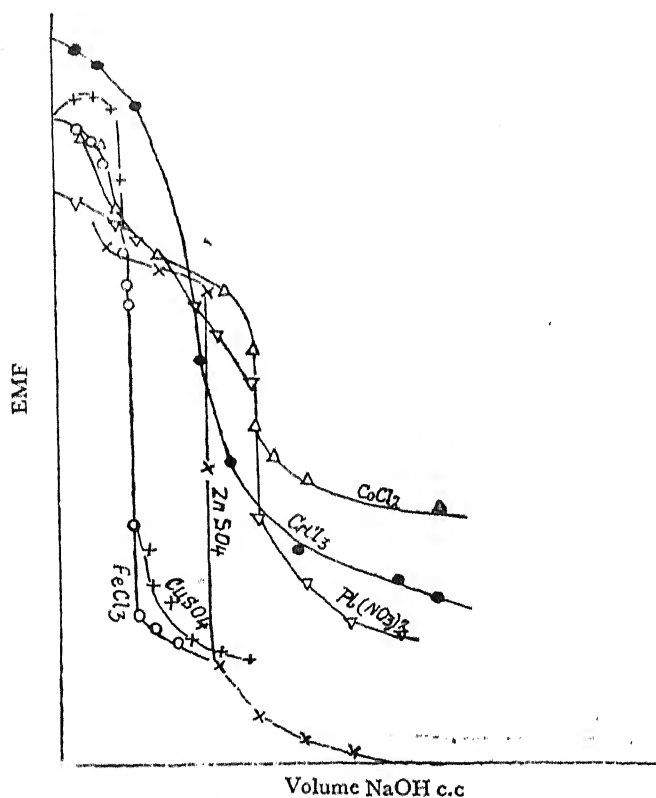


Fig. 3. Precipitation with NaOH

Since we did get good graphs in the titration of acids with alkalis, we felt that it might be worth-while to measure the pH of some buffers with this electrode after calibrating it empirically with a known solution like a glass electrode.

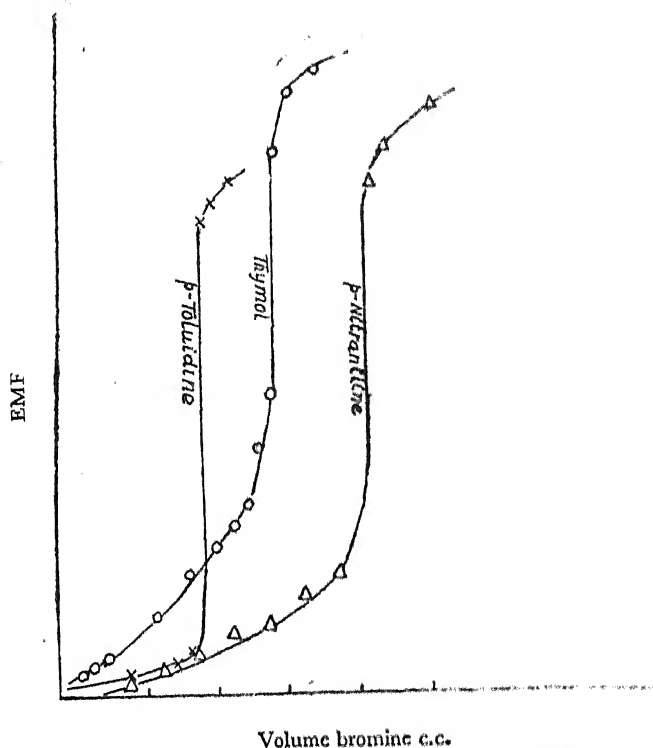
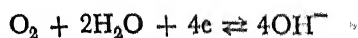
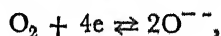


Fig. 4. Titration of organic substances with bromate-bromide mixture.

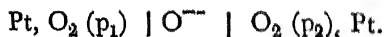
The theoretical situation regarding the functioning of a platinum electrode as a hydrogen electrode in absence of bubbled hydrogen is not quite clear. In fact, it is customary to think of the electrode in this condition, air or oxygen being freely accessible, as an oxygen electrode or an 'air electrode'.¹ Of course an oxygen electrode must indirectly function as a hydrogen electrode. But opinions appear to differ regarding details. Hoar² considers that the reaction at the electrode is



Glasstone³ writes the reaction more directly,



so that $-E_{\text{O}_2} = \frac{RT}{4F} \ln \frac{P_1}{P_2}$ corresponding to the cell



For an oxygen concentration cell, $\text{Pt}, \text{O}_2 \mid \text{O}^{--} (c_1) \parallel \text{O}^{--} (c_2) \mid \text{O}_2, \text{Pt}$: the EMF will of course be given by $\frac{RT}{2F} \ln \frac{c_1}{c_2}$. On the other hand, Kolthoff and

Laitinen (*loc. cit.* p. 96) write the reaction $O_2 + 2e \rightleftharpoons O^{--}$. But $O^{--} + H^+ \rightleftharpoons OH^-$. Then, $(O^{--}) = K^1 \frac{(OH^-)}{(H^+)} = K^1 \frac{K_w}{(H^+)} \cdot \frac{1}{(H^+)} = \frac{K^1 K_w}{(H^+)^2}$

$$\begin{aligned} \text{Now } E_{O_2} &= E_{O_2}^0 + \frac{RT}{2F} \ln \frac{pO_2}{(O^{--})} \\ &= E_{O_2}^0 + \frac{RT}{2F} \ln \frac{pO_2}{K^1 K_w} \times (H^+)^2 = \text{Const.} + .059 \log (H^+). \end{aligned}$$

If this mechanism is correct then the oxygen (or air) electrode should change its potential in the same manner with pH as a hydrogen electrode, and merely by determining this slope a decision cannot be made as to whether the electrode concerned is $Pt | H_2, H^+$ or $Pt | O_2, H^+$. To see how far the pH of a solution can be successfully measured with a bright platinum electrode, we prepared a series of buffer solutions. The electrode after due preparation was dipped in these solutions, the cell completed with a saturated calomel at the other end and the resulting EMF measured. Since the E_0 's of these electrodes are uncertain, the pH was calculated as follows. If E_1, E_2 are the concentrations corresponding to hydrogen ion concentrations pH_1, pH_2 respectively,

$E_2 - E_1 = 2.303 \frac{RT}{F} (pH_1 - pH_2)$. Knowing any one pH therefore the values for all other solutions may be calculated. We adopted a buffer of pH = 3.89 as the reference solution and calculated the pH of other mixtures with the following results.

TABLE 2
Measurement of pH with a bright platinum electrode.

pH actual	pH found	pH actual	pH found
0.65	2.25	3.98	3.96
1.09	2.34	4.00	4.20
1.42	2.36	5.20	5.50
1.99	2.39	7.00	7.16
3.09	2.92	8.90	8.83
3.89	3.89		

These measurements show that the pH of a buffer mixture may be estimated with tolerable accuracy in the range 3—9. Stable potentials are set up in 15 mins. Below pH 3 the electrode appears to be poorly sensitive to pH, changes and stable potentials are set up only after a long time. The results further show that the EMF—pH slope is given by $2.303 \frac{RT}{F}$ in the range specified, indicating that either the electrode functions directly as a hydrogen electrode or indirectly as such in accordance with the mechanism suggested by Kolthoff. It will be noted that the above formula is used with a glass electrode and eliminates the asymmetry error in E_0 . The experimental neatness in the present method is obvious and deserves further investigations with a view to improve the accuracy.

The electrode for these pH measurements was prepared by cleaning with hot chromic acid, washing and drying and finally glowing in a flame of methyl alcohol. The cleaning with chromic acid was necessary. In some other experiments the electrode was cleaned in conc. sulphuric or nitric acids, washed and used for the

measurement with poor results. Once the electrode had been cleaned in chromic acid an ethyl alcohol or acetone flame could be used instead of a methyl alcohol flame without change in the results. In one interesting experiment a thin layer of zinc was electrolytically deposited which was then washed and used for the measurement. It was found that the platinum electrode which is normally positive in this combination had become the negative end, and the bridge readings showed a drift even after a long time. The normal working was restored when the zinc had been dissolved away in sulphuric acid and the electrode glowed in a methyl alcohol flame. When the electrode was made a cathode in dilute sulphuric acid solution so that copious hydrogen was generated for a while the measurements again showed some variations from the correct values. On the other hand when oxygen was bubbled past the electrode for a while it did not produce appreciable departures from the correct values. These observations perhaps point out that the electrode works as an oxygen (air) electrode rather than a hydrogen electrode.

Some errors indicated in Table I are quite considerable, 2.5-3%. Perhaps they may be caused by slight changes in the standard electrode potentials during titration. This is emphasized by Richards⁴ who further points out from his investigations on the Pt/O₂ electrode that we are 'forced to picture the measured potentials as a compromise between a low oxidation potentials and the only partially attained O₂-O⁻ potential'. However, from the work described above and others in progress we are inclined to believe that by proper treatment of the platinum and attention to other details electrode potentials stable enough for accurate measurements may be secured.

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ATTERBERG'S CONSISTENCY LIMITS

Part I.—Relation between Plasticity—Index and Surface Area of Punjab Soils

By

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Atterberg^{1,2} was among the first to study the changes in the cohesive properties of soils as a function of moisture. The different consistencies were condensed to the following three essential forms :

- (a) *Upper Plastic Limit* or (Liquid Limit) is that moisture content at which the soil will barely flow under an applied force.
- (b) *Lower Plastic Limit* or (Plastic Limit) is that moisture content at which the soil can be rolled into a thread 0.125 inches in diameter without breaking.
- (c) *Plasticity number* or (Plasticity-Index) is the difference between the liquid and plastic limits.

Reeve⁸ had reported relationship between cation exchange capacity and specific area and the modulus of rupture of soils. The field capacity, moisture equivalent and 27.1 atm moisture relation values were found by Mortland⁶ to be related to the surface area of soils. The physical and chemical properties of any substance are, therefore, largely dependent upon the amount of particle surface exposed. Kelley and Jenny⁵ observed that grinding increased the cation exchange capacity of clays because of exposure of more exchange positions and an accompanying increase in surface area.

It is well known that montmorillonite has the highest base exchange capacity and surface area. Base exchange is much lower for Illite than for montmorillonite. The kaoline minerals with fixed crystal lattices, exhibit only slight hydration and adsorptive properties. Base-exchange or cation absorption and surface area are, therefore, very low for such type of soils.

The Atterberg constants are widely used in high way construction. The use of Atterberg constants is discussed in detail by Hogentogler⁴ and Spangler.⁹ The Airfield classification adopted by the United States Army in 1942 also places considerable stress on the plastic limits and plasticity index.

Very little work has so far been carried out on the relationship between surface area and other characteristics of soils. The present paper deals with the relation between the surface area and plasticity index of Punjab soils. This index is being largely used for the classification of soils.

EXPERIMENTAL

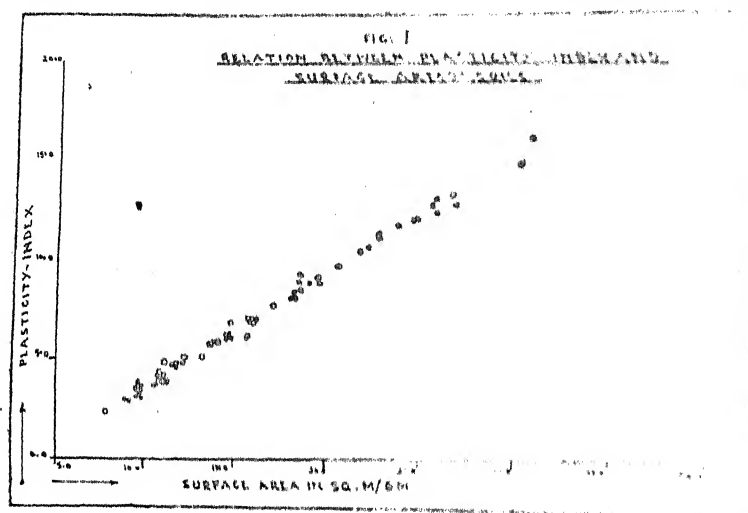
- (i) Seventy two soil samples taken from the different districts of the Punjab were selected for this investigation.
- (ii) The Atterberg consistency limits were determined by A.S.T.M. method.³
- (iii) Surface area was calculated by Orchiston's semi-empirical formula.⁷

$$S = \frac{18.06x}{0.337 - \log \log p/p_0}$$

where x is the amount of water adsorbed for 100 grams of dry soil at relative pressure p/p_0 .

DISCUSSION OF RESULTS

Fig. I indicated a very close relationship between the surface area and plasticity index of soils.



The correlation coefficient between plasticity index and surface area was found to be 0.9958, which was highly significant. The regression equation worked out was

$$Y = 4.336 + 1.649x$$

Where x stands for plasticity index and y stands for surface area of soils.

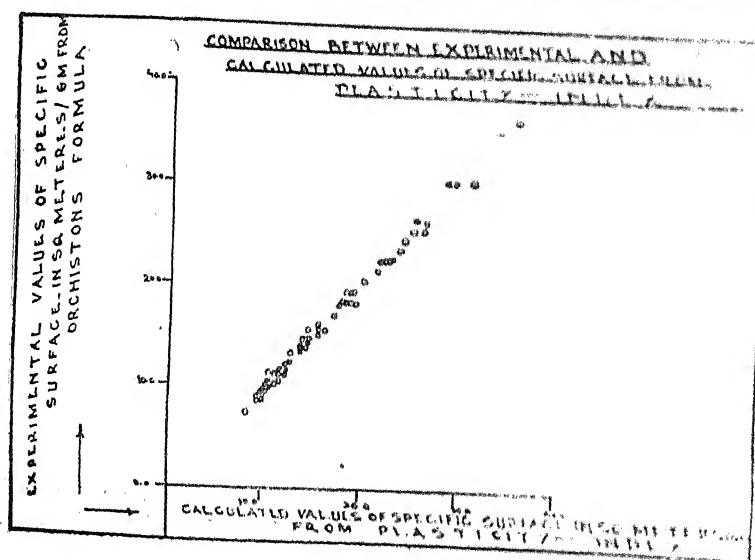


Fig. II

Fig. II showed the agreement between the experimentally determined values of plasticity index and those found from the above equation. The agreement was excellent.

It is well known that the physical properties of the clay depend to a large extent on the type of clay minerals that dominates the colloidal fraction. Therefore, knowing the surface area of soils of similar geological origin, one can easily guess the different physical properties, *i.e.*, plasticity index, base exchange etc. etc. From the above discussion it follows that in such regions where soils are of similar geological origin, the grain size characteristics (Surface area) can be used as a basis for judging the significant properties of the soils. The importance of this feature in soil mechanics can hardly be over estimated.

The Airfield classification adopted by the United States Army in 1942 places considerable stress on the plastic limits and plasticity index. The intimate relation obtained between the plasticity index and surface area of Punjab Soils affords us a new tool for judging the behaviour of soils in engineering. Thus knowing the specific surface of soils, the other constants can be determined. But these relationships are regional and need to be determined for other regions.

SUMMARY

- (i) Seventy-two representative Punjab Soils were analysed for the following characteristics.
 - (a) Atterberg's consistency Limits.
 - (b) Surface area.
- (ii) Statistical correlation was investigated between the plasticity index and surface area of soils. The correlation coefficient was -0.9958 , and highly significant.
- (iii) The intimate relationship between plasticity index and specific surface affords a new tool for assessing the engineering properties of soils.
- (iv) The above relationship is regional and needs to be investigated for soils of different geological formations in order to determine the limits of variations in different types of soils.

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SPECIFIC SURFACE FROM HEAT OF WETTING OF SOILS

By

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A dry soil evolves heat when placed in contact with water. This heat is termed heat of wetting. Rodewald¹⁵ recommended the following equation for representing the heat of wetting of the substances.

$$aF = E(r+i) \quad \dots \quad (1)$$

Where

- a = Work of adhesion per unit surface.
- F = Total surface of the wetting substance.
- E = Mechanical equivalent of heat.
- r = Heat equivalent to the work released by adhesion of water on the surface.
- i = Heat equivalent to the work needed to decrease cohesion between the particles.

Katz (ii) suggested the following equation :

$$W = \frac{A i}{B+i} \quad \dots \quad (2)$$

where

W = Heat produced when one gram of the dry swelling substance adsorbs one gram of water and A and B are constants.

The heat of wetting has been employed as an index of the colloidal activity of soils (i). Illin^{8,9} reported a relationship between heat of wetting of a solid in a non-reactive liquid and its particle size or surface area.

During the last twenty years, many methods based on the adsorption of gases at low temperatures^{3,4,5,6} capillary radii⁷, water adsorption isotherms¹³ and from the results of mechanical analysis have been proposed¹⁴ Mortland¹² proposed the following equation for the determination of specific surface of soils.

$$Y = 0.373x + 5.5 \quad \dots \quad (3)$$

Where

- X = Specific surface in sq. meters/gram.
- Y = Clay percentage.

But it has been observed that clay content of soils cannot be the sole criterion of surface area of soils,

The heat of wetting of soils can be a true index for characterising the physico-Chemical properties of soils.¹ Mortland (loc-cit) found an intimate relationship between the base exchange and the surface area of soils. Janert¹⁰ laid great stress on the heat of wetting for judging the physical properties of soils.

This investigation is concerned with the relationship between the heat of wetting and surface area of soils. The Chief merit of such a method would be that only one experimental value would be required for the determination of specific surface of soils.

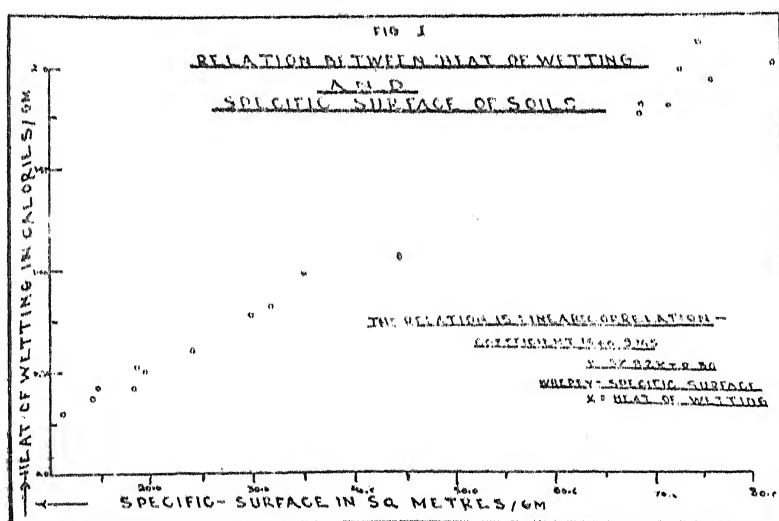
The heat of wetting of soils can be easily determined in a non-reactive, non-dissolving liquid in a wide mouth Dewar flask of about 1½ to 2.0 pints capacity, fitted with a Beckman thermometer.

EXPERIMENTAL

The values of heat of wetting and surface area of soils have been taken from the paper of Benjamin Makower, Shaw and Alexander.²

DISCUSSION OF RESULTS

Fig. I represents the relation between the heat of wetting and specific surface of soils. The correlation co-efficient was +0.9945, which was highly significant. The regression equation was :



$$Y = 37.82x + 0.80 \quad \dots \quad (4)$$

where

X = Heat of wetting in calories/gram

Y = Specific-surface in Sq. meters/gram.

Table I compares the values of heat of wetting determined experimentally and those calculated from the equation No. (4).

TABLE I

Comparison between the Experimental and the Calculated values of surface areas from heat of wetting of soils.

S. No.	Heat of wetting in Cal/Gm.	Surface area in sq. Meter/Gram.		Difference %
		Experimental from nitrogen adsorption —183°C	Calculated from equation No. 4	
1	0.29	11.2	11.77	+5.09
2	0.36	14.2	14.42	+1.55
3	0.41	14.6	16.30	+11.64
4	0.43	18.3	17.06	—6.71
5	0.50	19.1	19.71	+3.19
6	0.52	18.7	20.47	+9.46
7	0.61	24.0	23.87	—0.54
8	0.77	29.6	29.92	+1.08
9	0.82	31.9	31.81	—0.28
10	0.98	34.9	37.86	+11.48
11	1.06	44.4	40.89	—7.90
12	1.26	52.2	48.45	—7.18
13	1.28	51.4	49.20	—4.28
14	1.76	68.2	67.36	—1.23
15	1.81	71.1	69.25	—2.60
16	1.82	68.9	69.65	+1.09
17	1.94	75.7	74.17	—2.02
18	1.98	72.3	75.68	+4.67
19	2.04	82.0	77.95	—4.94
20	2.12	74.1	80.98	+9.28

A glance at the above table shows that there is a very close agreement between the experimental and the values calculated from equation No. (4).

$$y = 37.82 x + 0.80$$

$$\therefore \frac{dy}{dx} = 37.82$$

This means that the rate of change is constant i. e. with an increase of one calorie in the value of heat of wetting, the value of surface area increases by 37.82 sq. meters/gram.

The method, therefore, is capable for the evaluation of surface area of soils from one single value of the heat of wetting, which can be determined easily in the laboratory.

The relation between the heat of wetting and surface area of soils need to be determined for the different types of soils in various countries in order to find out the limits of variation of the above equation.

SUMMARY

(i) A very close relationship was obtained between the heat of wetting and surface area of soils. The equation of the curve was found to be

$$Y = 37.82 x + 0.80$$

where

X = Heat of wetting in calories/gram.

Y = Specific surface in sq. meters/gram.

Therefore the surface area of soils can be evaluated from one single value of the heat of wetting of soils.

(ii) The above relationship between heat of wetting and specific surface of soils should be verified for different types of soils in various countries for the determination of limits of variation of the above equation before adopting it for the estimation of surface area of soils.

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DECAY OF SHOCK WAVES IN A STELLAR ATMOSPHERE

By

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INTRODUCTION

At present it is believed that the ultimate observed stage of stellar evolution is that of a white dwarf. Under certain circumstances a gas cloud of inter stellar material contracts to form a proto star and finally a main sequence star. From the observations it is seen that at the main sequence stage stars can have masses of the order of fifty times the solar mass. Theoretically it is also proved that no star can reach the white dwarf stage with mass greater than of the order of 1.2 times the solar mass. Combining both these facts it can be safely concluded that in the course of evolution the stars spit out and feed back to the interstellar space quite an appreciable fraction of their masses.

Observationally also it is found that in several categories of stars in the outer layers unstable conditions do exist. In this connection following classes may be mentioned, Novae, P- cygni stars, Wolf Rayet stars, Planetary nebulae, Cepheids, β - Cepheids, flare and flash stars, Explosive dwarfs and several others. It may be noted in general that in some stars it is observed that the material moves away from the star, it is retarded and finally it falls back to the star (β Canis majoris stars and 48 Librae). In other cases only outward motion of the material is observed without any sign of falling in. In a number of cases the actual details of the motion of the material are not observed.

The actual cause and the mechanism leading to the cause for the various variations in the different kinds of stars mentioned above are not known. The present knowledge is not sufficient even to say definitely whether or not the same mechanism is responsible for all these observed unstable processes. In other words we do not actually know the details of the process by which a star gets rid of substantial portion of its mass during its evolution.

In the following cases observations do seem to suggest violent motions in the outer layers of the stars. Beals (1951) has shown that for most favourable circumstances for producing kind of P- cygni lines it is required that the atom receive a large initial impulse resulting in a maximum outward velocity before reaching the layers where self reversals occur. The phenomenon of doubling of lines in 17 Leporis (Struve 1942), β - Canis majoris stars (Odger 1955) and W- Virginia stars (Sanford 1952) suggests a violent out burst of gas from the atmosphere before the gas of the preceding outburst has fallen completely back and disappeared.

The best observed star in details is BW Vulpeculae. Its radial velocity was found variable (Hill 1930) with a range of 110 Km/sec. It was intensively observed by Petrie (1954). The amplitude of the velocity is found to be of the order of 200 Km/sec. By far the most striking feature of the radial velocity curves is their discontinuity. These curves show a jump from highest positive velocity to a "stand

still" and from "stand still" to the large negative velocity. There are some irregular motions observed for about fifteen or twenty minutes just at the start of the large velocity of approach before a smooth decelerated motion begins. Double lines are observed in the beginning and the end of the "stand still". There appear to be some minor disturbances even at the beginning of the "stand still".

From these observations it is quite clear that the radial velocity is not smooth but discontinuous. Due to some disturbances below the photosphere the material is thrown off outwards. This material falls back under gravity in some cases but there are other cases of some shell stars where this falling back is not observed at any time. From the studies of the stellar atmospheres it is found that the material density in these outer layers is very small or rather the gradient of density is large. Due to this fact any dynamical disturbance of even small amplitude on proceeding outwards from the photospheric regions can develop into a wave of large amplitude and ultimately into a wave of discontinuity.

From the present observations of BW Vulpeculae it is found that velocity of ejection, of the material, when corrected for the effects of foreshortening and limb darkening, is of the order of 130 km per second. The acoustic velocity in the same regions of the stellar atmosphere is given by

$$C^2 = \gamma \frac{k}{\mu H} T \quad \dots \quad (1)$$

where C is the sound velocity, γ is the effective ratio of the specific heats for the stellar material, μ is the mean molecular weight, T is the temperature k is Boltzmann constant and H is the unit of atomic weight. Using the appropriate values of these quantities on the right hand side of this equation for a B type star near the photosphere this sound velocity is found to be of the order of 23 km per second. When it is compared with the observed material velocity it is quite obvious that the motions in these stars are definitely of super sonic nature and consequently these are bound to develop into a wave of discontinuity. Thus these motions correspond to the dynamical effects of a shock wave in a stellar atmosphere. In the present note an attempt has been made to understand the radial velocity variations on this shock wave theory in a very rough approximation.

SHOCK WAVE THEORY

Most of the shock wave theory has been developed in connection with the explosives. Some experimental observations are also available from shock wave tube experiments. Certainly in all these cases the conditions are quite different than what they are in the stellar atmospheres. The relevant hydrodynamical equations can be obtained from the work of Brinkley and Kirkwood (1947). The following is the simplified account for the plane wave motion in the Lagrangian method.

Let ξ be the displacement at time t of a particle whose undisturbed position is x . Consider the material between planes at x and $x + \delta x$ at time $t = 0$. At time t the same material lies between planes at $x + \xi$ and $x + \xi + (\delta x + \frac{\partial \xi}{\partial x} \delta x)$.

The equation of continuity becomes

$$\rho \left(1 + \frac{\partial \xi}{\partial x} \right) = \rho_0 \quad \dots \quad (2)$$

where ρ_0 is undisturbed density and ρ is the density at any moment. Considering the forces acting on these bounding planes we get the following for the equation of motion.

$$\rho_0 \frac{\partial^2 \xi}{\partial t^2} = - \frac{\partial P}{\partial x} \quad \dots \quad (3)$$

If we have a situation such that P is a function of ρ only then the above equation can be written as

$$\frac{\partial^2 \xi}{\partial t^2} = \left(\frac{\rho}{\rho_0} \right)^2 \frac{dP}{d\rho} \frac{\partial^2 \xi}{\partial x^2} \quad \dots \quad (4)$$

now if u is the particle velocity then we have

$$u \equiv \frac{\partial \xi}{\partial t} \quad \dots \quad (5)$$

with this the equation (3) becomes

$$\frac{\partial u}{\partial t} = - \frac{1}{\rho_0} \frac{\partial P}{\partial x} \quad \dots \quad (6)$$

we can eliminate ξ between equations (5) and (2) and get

$$\left(\frac{\rho}{\rho_0} \right) \frac{\partial u}{\partial x} + \frac{1}{\rho C^2} \frac{\partial P}{\partial t} = 0 \quad \dots \quad (7)$$

where C is the sound velocity given by $(dP/d\rho)$.

These equations (6) and (7) form the basic equations which hold in the body of the fluid.

If we denote by p the excess of pressure over P_0 the undisturbed value we have

$$P = P_0 + p \quad \dots \quad (8)$$

then the above equations (6) and (7) take the form

$$\frac{\partial u}{\partial t} = - \frac{1}{\rho_0} \frac{\partial p}{\partial x} \quad \dots \quad (9)$$

$$\frac{\rho}{\rho_0} \frac{\partial u}{\partial x} + \frac{1}{\rho C^2} \frac{\partial p}{\partial t} = 0 \quad \dots \quad (10)$$

provided the variation of P_0 with respect to x is negligibly small in comparison with the variation of p with respect to x . This is an approximation but probably not too bad because in these layers of the stellar atmosphere the material pressure is already very small.

Besides these we also have the following equations relating the physical quantities on the two sides of the shock front.

Conservation of momentum gives

$$p = \rho_0 u U \quad \dots \quad (11)$$

Conservation of mass gives

$$\rho(U - u) = \rho_0 U \quad \dots \quad (12)$$

Enthalpy considerations lead to

$$\Delta H = -\frac{p}{2} \left(\frac{1}{\rho} + \frac{1}{\rho_0} \right) \quad \dots \quad (13)$$

where U is the velocity of the shock front and H is the specific enthalpy of the stellar material. ΔH is the increase in the specific enthalpy as a consequence of the material crossing the front. The actual details of the processes taking place within the shock front are not known with any certainty whatsoever. We only know the conditions of matter just before the shock front arrives at a point and also just after the passage of the shock. The above three relations are between these two situations. Zero suffix here refers to the pre-shock conditions and quantities without any suffix refer to post shock conditions.

Noting that

$$\frac{d}{dx} = \frac{\partial}{\partial x} + \frac{1}{U} \frac{\partial}{\partial t} \quad \text{and} \quad \frac{d}{dt} = \frac{\partial}{\partial t} + U \frac{\partial}{\partial x},$$

and operating on p using equation (11) we get

$$\frac{\partial u}{\partial t} + U \frac{\partial u}{\partial x} - \frac{K}{\rho_0} \frac{\partial p}{\partial x} - \frac{K}{\rho_0 U} \frac{\partial p}{\partial t} = 0 \quad \dots \quad (14)$$

where

$$K \equiv \rho_0 U \frac{du}{dp} = 1 - \rho_0 u \frac{dU}{dp} = 1 - \frac{p}{U} \cdot \frac{dU}{dp} \quad \dots \quad (15)$$

We need one more relation to solve for the four quantities $\frac{\partial u}{\partial x}$, $\frac{\partial u}{\partial t}$, $\frac{\partial p}{\partial x}$ and $\frac{\partial p}{\partial t}$.

This fourth relation is provided by the energy considerations. Consider the passage of the shock through a fluid. As it passes it leaves an increase in the internal energy corresponding to an increase in entropy as a consequence of passage through the shock front. This energy has to come out from the shock and hence the shock must decay. In the following this decay of the shock has been taken into account in a rough approximation.

Following Brinkley and Kirkwood (1947) the adiabatic work per unit area (on gas external to initial surface) is given by the expression

$$\int_{a_0}^x \rho_0 \Delta E \{p(\xi_0)\} d\xi_0 + \int_{t_0(x)}^{\infty} u' (p' + P_0) dt. \quad \dots \quad (16)$$

where u' and p' are particle velocity and excess pressure behind the shock front $t_0(x)$ is the instant of the arrival of the shock at x . $\Delta E(p)$ is the increase in specific internal energy of the gas at pressure P_0 and for an entropy increment corresponding to shock pressure p . a_0 is Lagrangian coordinate of the generating surface of the shock waves.

$$\int_{t_0(x)}^{\infty} P_0 u' dt = P_0 \Delta V + P_0 \int_{a_0}^x \left(\frac{\rho_0}{\rho} - 1 \right) d\xi_0 \quad \dots \quad (17)$$

where ρ is the final value of the fluid density and ΔV is the volume swept out by the generating surface. This is related to the specific enthalpy increment of the fluid traversed by the shock wave giving an excess of pressure over the initial pressure P_0 . Finally the fluid returns to the equilibrium value at the same pressure P_0 along a new adiabat. Let its specific enthalpy increment be denoted by $h(p)$ given by

$$h(p) = \Delta E + P_0 \Delta \left(\frac{1}{\rho} \right). \quad \dots \quad (18)$$

It can be shown that $h < \Delta H$, the specific enthalpy increment across the front. Using equations (17) and (18) the expression (16) reduces to

$$\int_{t_0(x)}^{\infty} p' u' dt + P_0 \Delta V + \int_{a_0}^x \rho_0 h(p(\xi_0)) d\xi_0 \rightarrow \int_{a_0}^x \rho_0 h(p(\xi_0)) d\xi_0 + P_0 \Delta V \quad (19)$$

because when $x \rightarrow \infty$ the first term tends to zero.

Hence subtracting we get

$$\int_{t_0(x)}^{\infty} p' u' dt = \int_x^{\infty} \rho_0 h(p(\xi_0)) d\xi_0. \quad \dots \quad (20)$$

This is treated as the fourth energy equation. Let us define the energy of the shock wave at x as equal to the work done on the gas exterior to x . Then we have

$$\begin{aligned} E_{sh} &= \int_{t_0(x)}^{\infty} p' u' dt \\ &= \int_x^{\infty} \rho_0 h(p(\xi_0)) d\xi_0 \\ &= S(x) \end{aligned} \quad \dots \quad (21)$$

This equation merely states that the rate at which the shock loses its energy equals to the rate at which the gas increase its total heat. Here it should be remarked that this picture is actually over simplified. In the real situation the shock

loses energy more than this because some portion of this energy is lost as the radiations. Because on account of the increase in temperature a lot of energy is absorbed in possible ionization of the material just at the passage of the shock. Then behind the shock recombination will take place giving rise to the radiations which may be lost to the system and we have not accounted for these losses in our equations. Here the situation is idealized as follows. The shock front is assumed to be transparent to the radiations. This assumption may not be very far from the reality because actually the front is a very thin layer which can be treated as a more abrupt discontinuity. The second assumption is that due to the great rise of temperature across the front the radiation flux which is proportional to the fourth power of the temperature is very fast and this tends to equalize the temperatures on both sides of the front almost instantaneously. This assumption is certainly not physically quite correct but it is hoped that it would not alter the general character of our solution here. In another paper (Odgers and Kushwaha 1959) a situation was considered where this transition across the front takes place in such a way that on two sides of the front isothermal relations between pressure and density hold. In the present note it is taken that on crossing the front the fluid lands on a different adiabatic and then on wards it follows the same adiabatic till it comes to the equilibrium state. The temperature variation has been neglected and also the radiation pressure is not taken into account. With these limitations in view we proceed as follows.

We evaluate the integral $\int_{t_0(x)}^{\infty} p'u' dt$ as follows :

$$\begin{aligned}\int_{t_0(x)}^{\infty} p'u' dt &= pu \int_{t_0(x)}^{\infty} \frac{p'u'}{pu} dt \\ &= pu \sigma \int_0^{\infty} \frac{p'u'}{pu} dT\end{aligned}$$

$$\therefore S(x) = pu \sigma \chi \quad \dots \quad (22)$$

where

$$T = \frac{t - t_0(x)}{\sigma} \quad \dots \quad (23)$$

and

$$\chi = \int_0^{\infty} \frac{p'u'}{pu} dT \quad \dots \quad (24)$$

$$\therefore -\frac{1}{\sigma} = -\frac{pu\chi}{S(x)} \quad \dots \quad (25)$$

It may be noted that we require the initial value of $\frac{p'u}{\rho u}$ as unity and its initial slope as -1 . It gives the following relation :

$$-\frac{1}{\sigma} = \frac{1}{p'u'} \frac{\partial}{\partial t} (p'u') \Big|_{t=t_0(x)} \quad \dots \quad (26)$$

Thus we have

$$-\frac{pu\chi}{S(x)} = \frac{1}{p} \cdot \frac{\partial p}{\partial t} + \frac{1}{u} \cdot \frac{\partial u}{\partial t} \quad \dots \quad (27)$$

Thus equations (6, 7, 14, and 27) form the four basic equations.

In the present note we are concerned with the actual decay of the shock as it proceeds in space. That is we wish to compute the variations of p with x .

We have

$$\frac{dp}{dx} = \frac{\partial p}{\partial x} + \frac{1}{U} \cdot \frac{\partial p}{\partial t} \quad \dots \quad (28)$$

Substituting for the partial derivatives on the right in the last equation we get

$$\frac{dp}{dx} = -\frac{\chi}{S(x)} \cdot \frac{1}{\rho_0 U^2} \cdot \frac{f}{2(k+1)} - f p^3 \quad \dots \quad (29)$$

where

$$f = 1 - \left(\frac{\rho_0 U}{\rho C} \right)^2 = 1 - \left(\frac{U}{C} - \frac{p}{\rho_0 C U} \right)^2 \quad \dots \quad (30)$$

$$k = \rho_0 U \frac{du}{dp} = 1 - \frac{p}{U} \cdot \frac{dU}{dp} \quad \dots \quad (31)$$

Also from equation (21) we have

$$\frac{dS(x)}{dx} = -\rho_0 h \{ p(\xi_0) \} \quad \dots \quad (32)$$

Finally, therefore, we have to integrate the two simultaneous equations (29) and (32).

EQUATIONS OF THE PROBLEM

Let the state of gas before the passage of the shock be described by the suffix zero. The unprimed quantities describe the state on just crossing the shock front and the starred quantities correspond to the final equilibrium state when the pressure reaches the value P_0 , the original value of the undisturbed state. The strength of the shock s at a point is defined by the following relation between the excess of pressure and the pressure before the passage of the shock.

$$p = sP_0 \quad (33)$$

Behind the shock the gas follows the same adiabatid.
Hence we have

$$\frac{P}{P_o} = \left(\frac{\rho}{\rho^*} \right)^\gamma = 1 + s \quad \dots \quad (34)$$

For ideal gas we have the relation

$$\left. \begin{aligned} P &= (\gamma - 1) \rho E \\ \text{and} \quad H &= E + \frac{P}{\rho} \end{aligned} \right\} \quad \dots \quad (35)$$

where H is the specific enthalpy.

Therefore this total gain in enthalpy is given by

$$H^* - H_o = \frac{\gamma}{\gamma - 1} P_o \left(\frac{1}{\rho^*} - \frac{1}{\rho_o} \right) = h \quad \dots \quad (36)$$

But for across the front we also have

$$\Delta H = \frac{p}{2} \left(\frac{1}{\rho} + \frac{1}{\rho_o} \right) \quad \dots \quad (37)$$

We can also write

$$H - H_o = \frac{\gamma}{\gamma - 1} \left(\frac{P}{\rho} - \frac{P_o}{\rho_o} \right) \quad \dots \quad (38)$$

Equating (37) and (38) we have

$$\frac{s}{2} (1 + Z) = \frac{\gamma}{\gamma - 1} (1 + s - Z) \quad \dots \quad (39)$$

where

$$Z = (\rho/\rho_o) \quad \dots \quad (40)$$

For the present case we can express the quantities behind the shock front in terms of the strength, s , as follows :

$$U = C_o (\sqrt{2\gamma + (\gamma + 1)s} / \sqrt{2\gamma})$$

$$k = 1 - (\gamma + 1)s / [2 \{ 2\gamma + (\gamma + 1)s \}]$$

$$f = 1 - \frac{2\gamma + (\gamma - 1)s}{2\gamma(1 + s)}$$

$$C^2 = C_o^2 \frac{(1 + s)[2\gamma + (\gamma - 1)s]}{2\gamma + (\gamma + 1)s}$$

$$p = s P_o$$

$$\rho = \rho_o \frac{2\gamma + (\gamma + 1)s}{2\gamma + (\gamma - 1)s}$$

$$h(p) = \frac{\gamma}{\gamma-1} \cdot \frac{\dot{P}_0}{\rho_0} \left[\frac{(\gamma-1)s + 2\gamma}{(\gamma+1)s + 2\gamma} (1+s)^{1/\gamma} - 1 \right]$$

$$u = \frac{C_0}{\sqrt{2\gamma}} \frac{2s}{\sqrt{2\gamma + s(\gamma+1)}}$$

where C is the velocity of sound.

Substituting these quantities in the equations (29) and (32) we get

$$\frac{dS}{dx} = - \frac{\gamma}{\gamma-1} P_0 \left[\frac{2\gamma+s(\gamma-1)}{2\gamma+s(\gamma+1)} (1+s)^{1/\gamma} - 1 \right] \quad (42)$$

$$\frac{ds}{dx} = - \frac{\chi}{S} P_0 2(\gamma+1) \frac{s^4}{[(5\gamma-1)(\gamma+1)s^2 + 4\gamma(5\gamma+1)s + 16\gamma^2]} \quad (43)$$

Let us define ξ and y by the following equations

$$S \equiv R_0 P_0 \xi \quad (44)$$

$$x = y R_0 \quad (45)$$

where R_0 is the radial distance of the point where the shock becomes observable initially from the centre of the star. The equations (42) and (43) with the help of equations (44) and (45) are reduced to the following equations in terms of non-dimensional variables.

$$\frac{d\eta}{dy} = - \frac{2\gamma + (\gamma-1)s}{2\gamma + (\gamma+1)s} (1+s)^{1/\gamma} \quad (46)$$

$$\frac{ds}{dy} = - \frac{\chi}{\eta+y} \cdot \frac{2(\gamma^2-1)}{\gamma} \cdot \frac{s^4}{[(5\gamma-1)(\gamma+1)s^2 + 4\gamma(5\gamma+1)s + 16\gamma^2]} \quad (47)$$

where η is defined as follows :

$$\frac{\gamma-1}{\gamma} \xi - y = \eta. \quad (48)$$

STARTING VALUES

To start the integrations of the equations (46) and (47) we have to choose the numerical values for the individual cases. Obviously $\gamma = 5/3$ for the atmospheres of the hot B stars because in these almost all the hydrogen is ionized. To get the other numerical values we have to use the specific observations of a particular star. In the present note the observational data for BW Vulpeculae has been used. There is no direct way of determining χ . It has to be estimated from the equation (24). The best estimates so far available from the previous work is the value of $2/3$. The same value is used in the present work also.

The initial value of S is obtained from the definition

$$S = \int_{t_0(x)}^{\infty} p' u' dt.$$

If we take the shock front as transparent then we can assume that whatever velocity we observe is the integrated velocity of the material in motion behind the shock. There is some uncertainty involved in evaluating this integral because

the value of p' is not observed. Only thing we know is that just behind the shock the pressure increase is sP_0 and finally at $t = \infty$ the pressure again returns to the equilibrium value P_0 . Hence to calculate this integral some arbitrary average value has been used and thus it can be taken out of the integral sign. It is quite obvious that in the beginning just after the shock the time gradient of pressure is very large and finally it becomes very small. From the forms of p, t , curves obtained in the laboratory a reasonable average value of p' can be guessed. In the present calculations this average value of p' is taken as ten times the equilibrium pressure P_0 . Finally this integral is evaluated by integrating the velocity curve of BW Vulpeculae. It turns out that the value of ξ is unity at she start.

The initial value of the strength s is obtained from the observed initial velocity for the star. The sound velocity is known from the temperature of the star. For the present star the Mach - number is about six and the initial value of the strength s is taken as eighty.

With these starting values the equations (46) and (47) were integrated numerically with the help of an electric desk calculator to the point where the material velocity is reduced to subsonic velocity because then the shock becomes observationally almost ineffective. The method used for numerical integration was the same as explained by Härm and Schwarzschild (1955). It follows the following scheme :

$$f(y + \Delta y) = f(y) + \Delta y \frac{df}{dy} + \frac{1}{2} D^1 (y + \frac{1}{2} \Delta y) - \frac{1}{12} D^2 (y) - \frac{1}{24} D^3 (y - \frac{1}{2} \Delta y) \quad \dots \quad (49)$$

where f is any function of y and D operators are the successive differences of $\Delta y (df/dy)$. The step value Δy is chosen suitably small so that even the second difference is negligibly small. The values of df/dy are obtained from the differential equations at any point. The differences are obtained by guessing at each step and finally checking them with the value obtained from the differential equations at the next point. If the check is not obtained the process is repeated till it checks within ± 1 in the last decimal figure. The following table gives the run of η and s at different points along the radius, starting point being the position where the shock is first observed.

y	η	s	U/C_0	u/C_0
1.00	-0.60	80	8.1	6.0
1.01	-0.64	70	7.6	5.6
1.02	-0.67	62	7.1	5.2
1.03	-0.70	55	6.7	4.9
1.04	-0.73	49	6.3	4.6
1.05	-0.76	44	6.0	4.4
1.06	-0.78	40	5.7	4.2
1.07	-0.81	36	5.5	4.0
1.08	-0.85	33	5.3	3.8
1.09	-0.85	31	5.0	3.6

y	η	s	U/G_0	u/G_0
1.10	-0.88	28	4.9	3.5
1.11	-0.90	26	4.7	3.3
1.12	-0.92	24	4.5	3.2
1.13	-0.94	22	4.3	3.1
1.14	-0.96	21	4.2	3.0
1.15	-0.98	19	4.1	2.9
1.16	-0.99	18	4.0	2.8
1.17	-1.01	17	3.8	2.6
1.18	-1.03	16	3.7	2.6
1.19	-1.05	15	3.6	2.5
1.20	-1.06	14	3.5	2.4
1.21	-1.08	13	3.4	2.3
1.22	-1.09	12	3.3	2.2
1.23	-1.11	12	3.2	2.2
1.24	-1.12	11	3.1	2.1
1.25	-1.14	10	3.1	2.1
1.26	-1.15	10	3.0	2.0
1.27	-1.17	9	2.9	1.9
1.28	-1.18	9	2.9	1.9
1.30	-1.21	8	2.7	1.8
1.32	-1.23	7	2.6	1.7
1.34	-1.26	7	2.5	1.6
1.36	-1.38	6	2.4	1.5
1.38	-1.31	6	2.4	1.5
1.40	-1.33	5	2.3	1.4
1.45	-1.39	5	2.2	1.3
1.50	-1.45	4	2.0	1.2
1.55	-1.55	4	2.0	1.1
1.60	-1.56	3	1.9	1.0
1.65	-1.61	3	1.8	0.9
1.70	-1.67	2	1.7	0.8
1.75	-1.72	2	1.7	0.8
1.80	-1.77	2	1.6	0.8
2.00	-1.98	2	1.5	0.6
2.2	-2.18	1	1.4	0.5
2.4	-2.38	1	1.4	0.5
2.6	-2.59	1	1.3	0.4
2.8	-2.79	1	1.3	0.4

CONCLUSION

From the table it is quite obvious how the shock decays in strength over the distance it travels. Following few points can be noted. The shock becomes visible at a certain depth from the surface of the star. The distance of this point from the centre in terms of the stellar radius would always be a fraction very near unity. By the time the shock decays it covers a distance nearly one and a half times the radius of the star. This fact may be possible in the case of shell stars which have the shell radius several times the stellar radius but for these hot stars like the present it does not seem to be possible. Knowing the run of the velocity of the shock front one can make some estimates of the time required for the effective decay of the shock under the present scheme. Taking a reasonable value of the fraction mentioned above and knowing the radius of the present star it is found that this decay will involve a time of the order of several days. Observationally also these two facts do not agree. The period of variation of velocity is only few hours and the range of the whole disturbed region of the atmosphere is only of the order of a tenth of the radius of the star. On both these accounts it can easily be concluded that according to the present scheme the decay of the strength of the shock is too slow to explain the observed facts about the radial velocity variations of BW Vulpeculae.

Elsewhere (Odgers and Kushwaha 1959) a similar investigation is carried out for the case where it is postulated that although the temperature on crossing the shock front increases by a large factor, the radiation flux due to this increase of temperature becomes very larger in those layers and the temperature is equilized very fast so that in effect for calculating the decay of the shock strength the isothermal transition relations will hold. There it is seen that the agreement between the theoretical velocity curve and the observed velocity curve is fairly good over the region on which shock effectively decays. These two investigations together seem to indicate fairly well that the true condition in the atmosphere of the star in question is very near the isothermal case rather than the adiabatic case.

It may be noted that no attempt is made to suggest any probable mechanism for the origin of these shock waves. The only assumption is that howsoever the shock is produced, it is produced below the photosphere and it becomes visible as it travels towards outer layers of the star.

In the end the author wishes to express his thanks to Dr. Odgers, G. J., for the very fruitful discussions in the initial stage of this paper.

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PHYSICO-CHEMICAL STUDY OF THE COMPLEX FORMATION OF BERYLLIUM IONS WITH ORGANIC LIGANDS—PART II. WITH OXINE

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ABSTRACT

A distinct yellow colour is obtained when an alcoholic solution of Oxine is added to an aqueous solution of Be^{2+} . The absorption spectrum of the mixture shows a maxima at 410 m μ indicating the presence of one complex. The stoichiometry of the components was determined by Job's continuous variation method by employing the absorption spectra data and was found to be 1 : 2. The dissociation constant of the complex was also determined by Job's method by using non equimolecular solutions and was found to be 2.296×10^{-3} at 28°C. A mechanism of the complex formation has also been given.

Separation of beryllium and aluminium by the use of oxine has been studied by several workers.¹ Kolthoff and Sandell² have used ammonium acetate before adding oxine while Neissner³ recommends the addition of a hot solution of oxine before adding ammonium acetate. Kerley⁴ has added acetic acid along with ammonium acetate. Leibowitz and Young⁵ have also shown that this method of separation is correct when aluminium is in excess. These workers had the basic view that aluminium forms an insoluble complex oxinate with oxine while beryllium does not form any complex. Recently it has been reported⁶ that a product of unknown composition is obtained by the interaction of beryllium ions and oxine in a controlled pH system. It therefore seems that no systematic physico-chemical approach has been made to study the actual nature of complex formation between Be^{2+} and oxine.

The authors have briefly reported⁷ the complex formation between Be^{12} and oxine. The detailed results of this investigation are discussed here.

EXPERIMENTAL

E. Merck sample of beryllium sulphate, which on analysis for Be (as its oxide) and SO_4 (as Barium Sulphate) found to be $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$, was used. Also AnalaR sample of 8-Hydroxy-Quinoline (oxine) was used. Aqueous solution of oxine in glacial acetic acid produces a yellowish red colour and an alcoholic solution of oxine has no colour at all. Therefore, an alcoholic solution of oxine was preferred to the acetic acid solution. It was found that when oxine is added to different amounts of beryllium sulphate it produces light yellow to greenish yellow colour depending upon the concentration of the beryllium solution used.

The spectrophotometric measurements were carried out by a Coleman Universal Spectrophotometer, Model 14 with matched cuvettes of 20 ml. capacity.

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To 2 c. c. of M/10 beryllium sulphate was added 20 c. c. of M/10 oxine and the absorption spectra of the mixture was studied in the visible region, from 380 m μ to 780 m μ . It was observed that a maxima in optical density is observed at 410 m μ (Table I below).

TABLE I

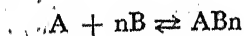
(Absorption spectra of 2 c. c. of M/10 BeSO₄ + 20 c. c. of M/10 Oxine).

Wavelength employed	Optical density	Wavelength employed (m μ)	Optical density
380	1.300	590	0.046
390	1.580	600	0.044
400	1.660	610	0.042
410	1.690	620	0.030
420	1.640	630	0.028
430	1.330	640	0.026
440	0.955	650	0.024
450	0.740	660	0.023
460	0.556	670	0.021
470	0.439	680	0.021
480	0.324	690	0.021
490	0.261	700	0.020
500	0.211	710	0.022
510	0.171	720	0.023
520	0.139	730	0.024
530	0.110	740	0.025
540	0.089	750	0.032
550	0.072	760	0.038
560	0.059	770	0.046
570	0.049	780	0.060
580	0.047		

This clearly points towards a complex formation between beryllium sulphate and oxine. It has been found that an aqueous solution of beryllium sulphate has no absorption in the visible region and also an alcoholic solution of oxine has got practically negligible absorption. All the measurements were made at the room temperature, 28°C.

Stoichiometry of the Components.—The actual nature of the complex formation was studied by Job's continuous variation method.⁸ The method in general is as follows :

If any metallic ion A reacts with n molecules of B to form a complex AB_n then the equilibrium between them shall be—



Applying the Law of Mass Action—

$$K = \frac{(AB_n)}{(A)(B)^n}$$

The different sets of solution used for this method were similar to the beryllium oxalate system described in a previous communication.⁹ The main

point being that the solutions are equimolecular and the total volume is kept constant. Therefore, the restriction imposed, in general, is—

$$(A) + (B) = C \text{ where } C \text{ is a constant.}$$

When the concentration of ABn is maximum, then—

$$(B)/(A) = n$$

$$\text{or } \frac{d(ABn)}{d(A)} = 0$$

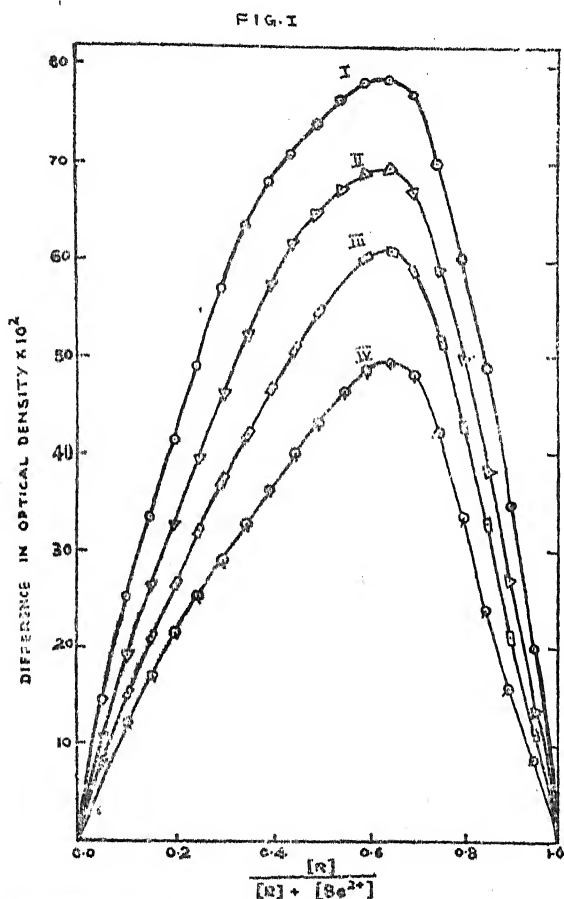
In other words, for a constant total concentration of metal and chelating agent, the concentration is greatest when the metal and chelating agent are brought together in the same ratios in which they exist in the chelate.¹⁰ In our case, as already mentioned, the chelate is the only coloured substance present having appreciable absorption. Therefore, the optical density of the solution is proportional to chelate concentration. Hence a plot of optical density versus composition of the solution would give a maximum at the composition corresponding to the formula of the chelate. Vosburgh and Copper¹¹ have suggested that instead of composition it is better to plot the ratio $\frac{[R]}{[R] + [M]}$ where (R) is the concentration of the organic ligand employed and (M) is the concentration of the metallic ion. In Fig. I curves I—IV it will be seen that we have employed the above method.

We have investigated different sets of solutions of M/10 beryllium sulphate and M/10 Oxine at wavelengths of 400, 450, 480, 500 and 550 m μ (Table II).

TABLE II
(Absorption Spectra of M/10 BeSO₄ and M/10 Oxine).

Volume of M/10 BeSO ₄ in ml.	Volume of M/10 Oxine in ml.	Optical densities at				
		400 m μ	450 m μ	480 m μ	500 m μ	550 m μ
20	0	0.039	0.025	0.017	0.006	0.001
19	1	1.190	0.228	0.144	0.024	0.014
18	2	1.460	0.360	0.253	0.031	0.016
17	3	1.540	0.490	0.353	0.043	0.018
16	4	1.590	0.612	0.416	0.060	0.021
15	5	1.630	0.758	0.492	0.078	0.024
14	6	1.650	0.860	0.573	0.102	0.027
13	7	1.670	0.960	0.637	0.132	0.029
12	8	1.680	1.010	0.682	0.155	0.031
11	9	1.690	1.070	0.711	0.179	0.033
10	10	1.690	1.114	0.739	0.190	0.036
9	11	1.690	1.120	0.765	0.200	0.039
8	12	1.700	1.125	0.783	0.208	0.045
7	13	1.700	1.270	0.790	0.213	0.049
6	14	1.690	1.250	0.773	0.203	0.049
5	15	1.680	1.130	0.002	0.198	0.047
4	16	1.670	1.001	0.604	0.186	0.044
3	17	1.660	0.920	0.493	0.169	0.040
2	18	1.630	0.810	0.349	0.139	0.037
1	19	1.500	0.635	0.200	0.109	0.033
0	20	0.178	0.060	0.050	0.044	0.026

As is evident from Table II the wavelength of $480\text{ m}\mu$ gives most satisfactory readings and was therefore selected for the whole series of measurement. Further measurements have been done with M/20, M/30 and M/40 solution of each of Beryllium sulphate and oxine at $480\text{ m}\mu$. The graphs between optical density and the ratio $(R)/(R) + (\text{Be}^{2+})$ have been plotted in Fig. I curves I—IV. All the curves have the same maxima at 1 : 2 ratio of the metal ion and the organic ligand. Similar results can also be obtained if we take any other wavelength but the one chosen ($480\text{ m}\mu$) gives the best results.



Curve I : $\text{BeSO}_4 = 0.10\text{ M}$; Oxine = 0.10 M

II : $\text{BeSO}_4 = 0.05\text{ M}$; Oxine = 0.05 M

III : $\text{BeSO}_4 = 0.033\text{ M}$; Oxine = 0.033 M

IV : $\text{BeSO}_4 = 0.025\text{ M}$; Oxine = 0.025 M

Calculation of the dissociation constant.—The dissociation constant was calculated by the Job's method (*loc. cit.*) and as described previously by the authors⁹ the enlarged equation was employed. As before, non-equimolecular solutions were prepared and graphs between optical density and the amount of ligands employed have been plotted. The maxima in the curve was taken as the value of x . Here

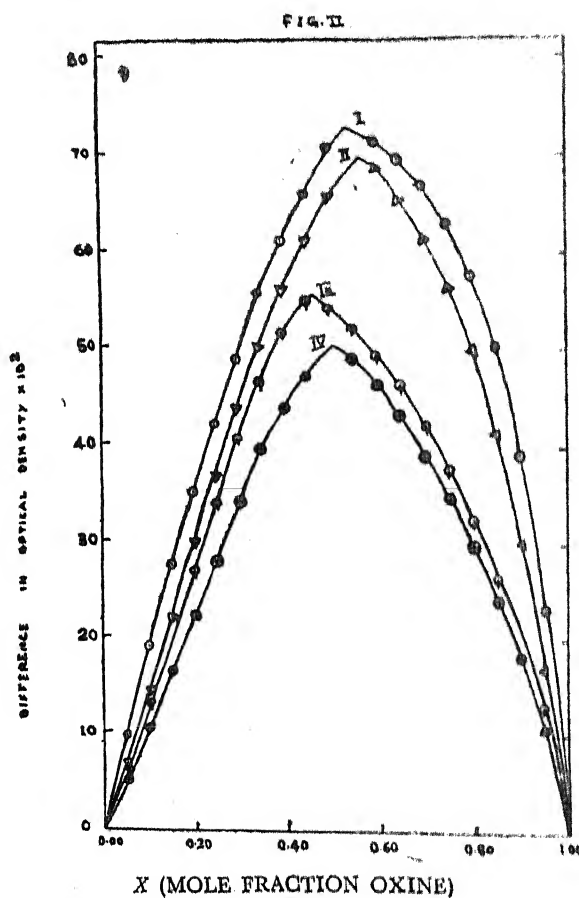
he equation assumes slightly different form as $m = 1$ and $n = 2$. Therefore it becomes :

$$c^{1+2-1} p^{2-1} [(p+2)x-2]^{1+2} = K[1^{2+1} 2^{1-1} (p-1)^{1+2-1} \{2-(1+2)x\}],$$

$$\text{or } c^2.p [(p+2)x+2]^3 = K(p-1)^2.(2-3x),$$

$$\text{or } K = \frac{c^2 p [(p+2)x-2]^3}{(p-1)^2 (2-3x)}$$

Thus the dissociation constant is obtained by putting the values of c , p and x where c stands for the concentration of beryllium, p stands for the concentration of the ligand and x for the amount of ligand used. The results of different sets as obtained from Fig. II curves I—IV have been tabulated below :



Curve I : $c = 0.10$; $p = 2.50$; $x = 0.540$

II : $c = 0.10$; $p = 2.00$; $x = 0.578$

III : $c = 0.05$; $p = 5.00$; $x = 0.460$

IV : $c = 0.05$; $p = 4.00$; $x = 0.511$

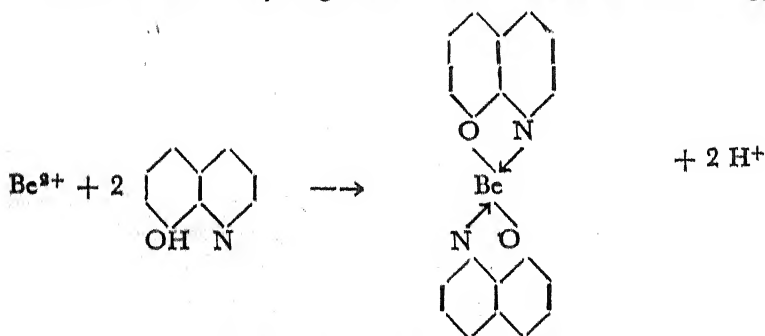
TABLE III
(Room temperature = 28°C)

Fig. No.	Curve No.	c	p	x	K _x 10 ³
II	I	0.10	2.50	0.540	2.325
II	II	0.10	2.00	0.578	3.284
II	III	0.05	5.00	0.460	2.289
II	IV	0.05	4.00	0.511	2.289

Thus the average value of the dissociation constant is 2.296×10^{-3} at 28°C

DISCUSSION

It is seen that there forms a 1 : 2 complex between beryllium ions and oxine, which has hitherto been not noticed. The hydroxyl group of the oxine gives off its labile hydrogen ion in solution and the lone pair of electrons associated with the nitrogen co-ordinates with the Beryllium ion. A distinct lowering of pH is obtained, similar to the one obtained in the case of beryllium o-Cresotate system¹² which supports the liberation of hydrogen ion. Therefore the reaction suggested is—



The above structure is supported by the following pH measurements (Table IV).

TABLE IV
System : 20 c. c. of M/10 BeSO₄ + Oxine.

M/2 Oxine added	pH of the system.
0.0 c. c.	3.62
0.5 c. c.	3.41
1.0 c. c.	3.32
1.5 c. c.	3.25
2.0 c. c.	3.16
2.5 c. c.	3.12
3.0 c. c.	3.10
3.5 c. c.	3.10
4.0 c. c.	3.23
4.5 c. c.	3.37
5.00 c. c.	3.48
6.00 c. c.	3.59
7.00 c. c.	3.63
8.00 c. c.	3.76
1.00 c. c.	4.12

As is evident from the above table, there is a marked fall of pH from 3.62 to 3.10 and then again on increase which is easily accounted by saying that the Oxine is in excess. Thus the above structure is justified.

The value of the dissociation constant obtained by taking the mean of all the concentration comes to be 2.296×10^{-3} at 28°C, which have been tabulated in Table III.

The authors express their grateful thanks to Prof. A. K. Bhattacharya for his kind interest and encouragement.

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ON BESSEL POLYNOMIALS

By

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The differential equation for a Bessel polynomial of order n is

$$x^2 \frac{d^2 y}{dx^2} + 2(x+1) \frac{dy}{dx} = n(n+1)y \quad \dots (1)$$

One of the solutions of (1) is $y_n(x) = \sum_{r=0}^n \frac{n!}{r!(n-r)!} \left(\frac{x}{2}\right)^r$

for positive integral values of n .

The function has been studied by H. L. Krau and O. Frink (1949), Emil Grosswald (1951) M. Nassif (1954), Al Salam (1957), Carlitz (1957), C. K. Chatterjee (1957). Here I will consider some properties of the function believed to be new.

Tarun's inequality, for other functions, has been considered by G. Szig (1948). Here, Tarun's inequality for this function is proved amongst other properties.

Theorem 1. $y_n^2(x) - y_{n+1}(x)y_{n-1}(x) \geq 0$ for all

real $x > 0$ and $n > 0$

Chatterjee (1957) proved that $\frac{d}{dx}(x^{2n+2} e^{-1/x})$

$$= x^{2n+2} e^{-1/x} y_n \text{ and } y_{n+1} = (2n+1)x y_n + y_{n-1}$$

$$\text{Hence } \frac{d}{dx} x^{2n+2} e^{-1/x} [y_n^2 - y_{n+1} y_{n-1}]$$

$$= x^{2n} e^{-1/x} (2n+1)x (y_n^2 - y_{n+1} y_{n-1}) - 2x^{2n+1} y_{n+1} y_{n-1}$$

$$\text{Let } \Delta x = x^{2n} e^{-1/x} [y_n^2 - y_{n+1} y_{n-1}].$$

$$\text{Then } \frac{d}{dx} \Delta x = -2 y_{n+1} y_{n-1} = 0 \text{ if } y_{n+1} \text{ or } y_{n-1} = 0$$

Chatterjee (1957) proved that $x^n y'_n = (nx-1)y_n + y_{n-2}$

and $x^2 y'_{n-1} = y_n - (nx+1)y_{n-1}$

Hence $\frac{d^2}{dx^2} \Delta x = \frac{2y_n^2(2n+1)}{x} > 0$ if $y_{n+1} = 0, x > 0, n > 0$

$$\frac{d^2}{dx^2} \Delta x = -\frac{(2n+1)}{x} \frac{2y_n^2}{x} < 0 \text{ if } y_{n-1} = 0, x > 0, n > 0,$$

Since it is evident that y_n, y_{n-1} cannot be equal to zero simultaneously.

It follows that Δn is a minimum or maximum according as $y_{n+1} = 0$ or $y_{n-1} = 0$ and $x > 0, n > 0$

Let α be a Zero of y_{n-1} . We have $\Delta x(\alpha) = \alpha e^{-1/\alpha} y_n^2(\alpha) > 0$,

since y_n, y_{n-1} have no common zero.

Similarly for a Zero of y_{n+1} also.

Therefore, $\Delta n(x) > 0$ at all its relative extrema on the x axis if $n > 0$. Hence the theorem.

Theorem 2. Tarun's inequality holds good for Bessel functions also.

We know that $\frac{d}{dz} z^n J_n = z^n J_{n-1}$ and $J_{n-2} + y_n = \frac{2(n-1)}{z} J_{n-1}$

If $\Delta n = J_n^2 - J_{n+1} J_{n-1}$ then $\frac{d}{dz} \Delta n = \frac{2}{z} J_{n+1} J_{n-1}$

Hence, as before, $\Delta n \geq 0$ for all real values of z if $z > 0$

Theorem 3. (1) $y_n = y_{n-1} + \sum_{r=1}^n e_r \cdot 1.3(2r-1)x^2 \times y_{n-1} - r$

$$(2) 2^n y^n \left(\frac{x}{\lambda} \right) = y_n \left(\frac{2x}{\lambda} \right) y_{-1} \left(\frac{2x}{\lambda} \right) + \sum_{r=1}^n e_r y_{n-r} \left(\frac{2x}{\lambda} \right) y_{n-1} \left(\frac{2x}{\lambda} \right)$$

W. Al-Salam (1957) proved that $\sum_{n=0}^{\alpha} y_{n-1}(x) \frac{t^n}{[n]} = e \frac{1-(1-2xt)^{\frac{1}{2}}}{x}$

$$\text{and } \sum_{n=0}^{\alpha} y_n(x) \frac{t^n}{[n]} = (1-2xt)^{-1/2} e \frac{1-(1-2xt)^{\frac{1}{2}}}{x}$$

$$\text{Hence } \sum_{n=0}^{\alpha} y_n(x) \frac{t^n}{[n]} = (1-2xt)^{-1/2} \sum_{n=0}^{\alpha} y_{n-1}(x) \frac{t^n}{[n]}$$

$$= [1 + xt + \frac{1.3}{2} x^2 t^2 + \dots] \sum_{n=0}^{\alpha} y_{n-1}(x) \frac{t^n}{[n]}$$

Hence the result (1) of Theorem 3.

$$\begin{aligned} \text{Again, } \sum_{n=0}^{\alpha} y_n \left(\frac{x}{\lambda} \right) \frac{\lambda^n t^n}{n!} &= (1-2xt)^{-1/2} \times \\ e^{\frac{\lambda}{x} [1-(1-2xt)^{1/2}]} &= (1-2xt)^{-1/2} e^{\frac{\lambda}{2x} [1-(1-2xt)^{1/2}]} \times \\ e^{\frac{\lambda}{2x} [1-(1-2xt)^{1/2}]} &= \sum_0^{\alpha} y_n \left(\frac{2x}{\lambda} \right) \left(\frac{\lambda t}{2} \right)^n \sum_0^{\alpha} y_{n-1} \left(\frac{2x}{\lambda} \right) \times \left(\frac{\lambda t}{2} \right)^n \end{aligned}$$

Hence the result (2) of Theorem 3.

$$\begin{aligned} \text{Theorem 4. (i)} \quad \sum_0^p (2n+1) y_n(x) y_n(y_1) \\ = \frac{y_{p+1}(x) y_p(y_1) + y_{p+1}(y_1) y_p(x) - y_{p-1}(x) y_0(y_1) - y_0(x) y_{-1}(y_1)}{x + y_1} \\ \text{(ii)} \quad \sum_0^p (2n+1) y_n^2(x) = \frac{y_{p+1}(x) y_p(x) y_0(x) y_{-1}(x)}{x} \end{aligned}$$

W. A. Al-Salam (1957) proved that

$$y_{n+1}(x) = (2n+1)x y_n(x) + y_{n-1}(x)$$

$$\text{Hence } y_{n+1}(x) = (2n+1)x y_n(x) + y_{n-1}(x),$$

$$y_{n+1}(y_1) = (2n+1)y_1 y_n(y_1) + y_{n-1}(y_1).$$

$$\begin{aligned} \text{Hence } (2n+1)(x+y_1)y_n(x)y_n(y_1) &= y_{n+1}(x)y_n(y_1) + y_{n+1}(y_1)y_n(x) \\ &\quad - y_{n-1}(x)y_n(y_1) - y_{n-1}(y_1)y_n(x) \end{aligned}$$

Hence the result (i) of Theorem 4. Putting $x = y_1$ we get the result (ii) of theorem 4.

$$\text{Theorem 5. If } f\left(\frac{1}{x}\right) = x \int_0^{\alpha} h(1+t) e^{-xt} dt$$

and $h(1+t)$ can be expanded in a series in Legunder's function then $f(x)$ can be expanded in a series in $y_n(x)$ if $x > 0, n > 0$

$$\text{Al-Salam (1957) proved that } y_n(x) = \int_0^{\alpha} P_n(1+t) e^{-t} dt$$

$$\text{Hence } y_n\left(\frac{1}{x}\right) = x \int_0^{\alpha} P_n(1+t) e^{-nt} dt$$

$$\text{If } f\left(\frac{1}{x}\right) = x \int_0^{\alpha} h(1+t) e^{-xt} dt = \sum_0^{\alpha} a_n x \int_0^{\alpha} P_n(1+t) \times e^{-xt} dt,$$

then $f(x) = \sum_0^{\alpha} a_n y_n(x)$.

Example. Let $h(1+t) = (1+t)^n$

then $f\left(\frac{1}{x}\right) = 1 + \frac{n}{x} + \frac{n(n-1)}{x^2} + \dots + \frac{1}{x^{n-1}}$

We know that $z^n = \sum_0^n a_{n-m} P_{n-m}(2)$

where $a_n = \frac{2^n (1/2)^n}{2^n}$, $a_{n-m} = 0$ when $n-m$ is odd or negative.

$$\text{and } = \frac{(2m+1) 2^m \frac{n}{2} \frac{n-m}{2}}{\frac{n-m}{2} \frac{n+m-1}{2}}$$

Hence $1 + nx + x(n-1)x^2 + \dots + \frac{1}{x^{n-1}} = \sum_0^n a_{n-m} y_n(x)$

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FORMATION OF COMPLEX COMPOUNDS BETWEEN CADMIUM HALIDES AND ALKALI HALIDES

Part IV.—System $\text{CdCl}_2 - \text{LiCl} - \text{H}_2\text{O}$

By

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ABSTRACT

The formation of complex compounds between cadmium chloride and lithium chloride has been studied by the conductivity, viscosity, freezing point, refractive index and pH methods. The graphs obtained show six breaks at exactly the same points indicating the formation of six complexes, namely, $\text{CdCl}_2 \cdot 4\text{LiCl}$, $\text{CdCl}_2 \cdot 2\text{LiCl}$, $2\text{CdCl}_2 \cdot 3\text{LiCl}$, $\text{CdCl}_2 \cdot \text{LiCl}$, $3\text{CdCl}_2 \cdot 2\text{LiCl}$ and $2\text{CdCl}_2 \cdot \text{LiCl}$ of which only $\text{CdCl}_2 \cdot \text{LiCl}$ has been reported by earlier workers, the other five being new compounds. The above results have been confirmed by light absorption method.

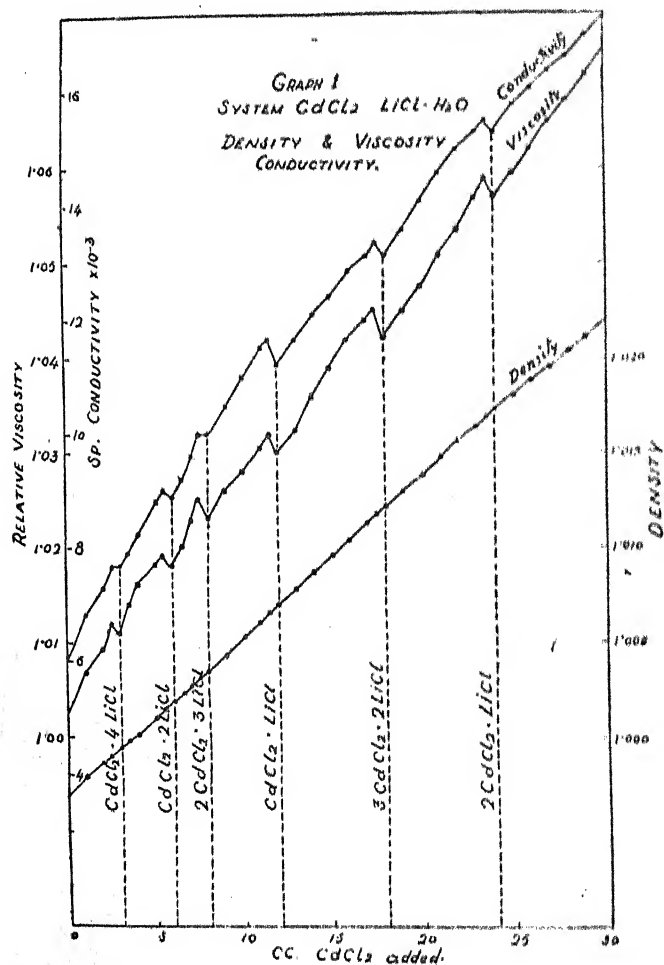
INTRODUCTION

In continuation of the work on the study of the formation of complex compounds between cadmium chloride and alkali chlorides the work was extended to the study of the system $\text{CdCl}_2 - \text{LiCl} - \text{H}_2\text{O}$. A survey of the literature shows that apart from the observation of A. Chassevant¹ who prepared hygroscopic needle-like crystals of lithium cadmium trichloride, $\text{LiCl} \cdot \text{CdCl}_2 \cdot 3.5\text{H}_2\text{O}$ or $\text{LiCdCl}_3 \cdot 3.5\text{H}_2\text{O}$ from a solution containing CdCl_2 : LiCl in the proportions 1:2 and found that the crystals can be dehydrated at 120° and that they are soluble in alcohol, no work has been done on the formation of complex compounds between cadmium chloride and lithium chloride. So it was thought worth while to investigate the system to find out the nature and number of complexes formed in aqueous solutions.

EXPERIMENTAL

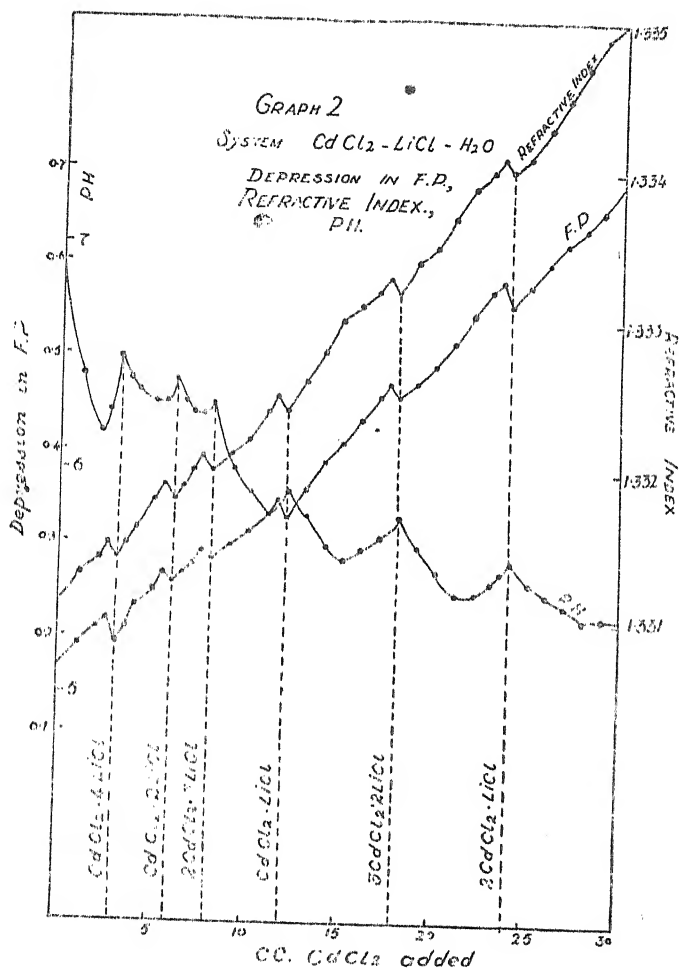
The substances used were of A. R. quality. Stock solutions of cadmium chloride and lithium chloride were prepared by dissolving the calculated amounts of the respective salts in conductivity water to form M/4 solutions. The method of monovariation of Nayar and Pande² which consists in keeping the concentration of one of the constituents constant and varying the other systematically was adopted to prepare the subsequent solutions. A 50 cc. standard flask was taken and 12 cc. of lithium chloride was run into it from a burette. The requisite volume of cadmium chloride was then added and the volumes made up to 50 cc. with conductivity water. In this way 39 mixed solutions were prepared in all of which the concentration of lithium chloride was kept constant while the other varied systematically from 0.0M to 0.150M (0.0cc. to 30.0cc.). The solutions were kept in steamed reagent bottles. These solutions were then subjected to careful study by conductivity, viscosity, freezing point, refractive index and pH measurements. The conductivity and viscosity measurements were carried out in an electrically maintained thermostat the temperature of which was kept at $30 \pm 0.05^\circ\text{C}$. The freezing points were determined by using the Beckmann F. P. apparatus. The temperature of the cooling

bath was maintained at $-5 \pm 1^\circ\text{C}$. by the addition of ice or salt as the case may be so as to avoid excessive super cooling. 10 cc. of the solution was used for each determination, the average of 3 determinations being taken as the correct one. The refractive index of each of the mixed solutions was measured by using an Abbe type of refractometer. To carry out the determinations at a constant temperature, water was allowed to flow through the hollow prism casings from a thermostat, the temperature of which was so adjusted that the water circulating through the refractometer was at 30°C . Care was taken to see that the prism was thoroughly clean and dry before a new solution was placed on it. The pH of all the mixed solutions were measured by using a Metrohm pH meter. The electrodes were calomel and glass electrodes manufactured by the same company. All measurements were carried out at the room temperature of about 27°C . The results of all the above measurements are shown graphically in graphs 1 and 2.



In order to confirm the results obtained by the above five methods recourse was taken to absorption spectra studies. The Beckmann spectrophotometer was used for the purpose. Those concentrations at which complexes were found to be

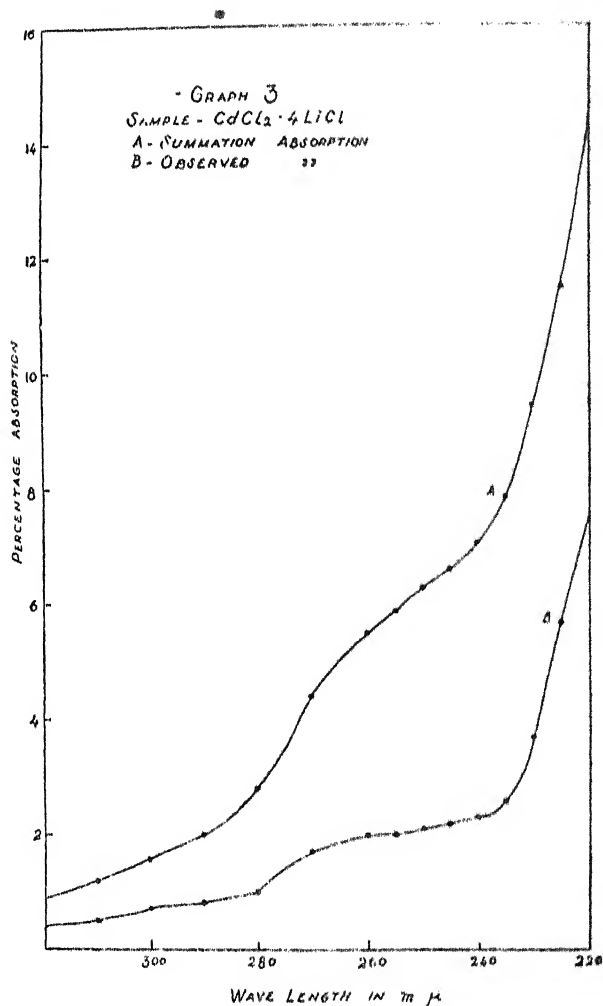
present have been taken up for the study. First the percentage absorption of the individual solutions and then those of the mixtures having the same concentrations of cadmium chloride and lithium chloride as in the individual solutions were determined in the range $320\text{ m}\mu$ to $220\text{ m}\mu$. Thus the absorption spectra of all the complexes present in the system was studied.



RESULTS AND DISCUSSION

The values of conductivity, density, viscosity, freezing point, refractive index and pH were plotted against the concentration of the variant, namely cadmium chloride (Graphs 1 and 2). In the case of density only a straight line was obtained. In all the other cases the curves showed six breaks at points corresponding to the ratio $\text{CdCl}_2 : \text{LiCl}$ as 1:4, 1:2, 1:1.5, 1:1, 1.5:1, and 2:1 showing the formation of the complexes $\text{CdCl}_2 \cdot 4\text{LiCl}$, $\text{CdCl}_2 \cdot 2\text{LiCl}$, $2\text{CdCl}_2 \cdot 3\text{LiCl}$, $\text{CdCl}_2 \cdot \text{LiCl}$, $3\text{CdCl}_2 \cdot 2\text{LiCl}$ and $2\text{CdCl}_2 \cdot \text{LiCl}$. Since all the different physico-chemical properties indicate the formation of the same number of complexes having the same compositions it can be concluded that the above mentioned six complexes are formed between cadmium chloride and lithium chloride in aqueous solutions.

Graph 3 shows the results of the absorption spectra studies of the complex $\text{CdCl}_2 \cdot 4\text{LiCl}$. The graphs are drawn between percentage absorption and wavelength. Curve A shows the percentage absorption of the mixture calculated on the basis of the additive rule assuming that no reaction takes place between the reactants. Curve B shows the actual observed absorption of the mixture. From the graphs it can be clearly seen that the absorption of the mixture is distinctly different from those calculated for no interaction. This deviation from the summation absorption



is explained as due to the formation of complexes between the reactants. Naturally the new product will have an absorption different from those of the individual salts or from those calculated for no reaction. The results of the absorption spectra studies of all the six complexes follow a similar course. So in order to economize space only one graph is given here. Thus all the different physico-chemical properties studied indicate that the above mentioned six complexes are formed between cadmium chloride and lithium chloride in aqueous solutions.

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